Evolution of the electronic structure of cyclic polythiophene upon bipolaron doping

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(January 11, 2022)

Abstract

Electronic structures of undoped and doped cyclic polythiophene (PT) are studied using modified σ-bond compressibility model. Cyclic PT doped with odd number of bipolarons creates an aromatic polyene backbone containing $(4n+2)$ π-electrons and the system is driven towards the quinoid form. Consequently, we find an insulator-metal transition for dopant concentration $\geq 14$ mol% and a $\sim 0.8$ eV redshift in Fermi energy at 30 mol%. For even number of bipolarons, we propose here that the form having two singly occupied degenerate orbitals will be stable in a sufficiently large cyclic PT.

PACS numbers : 79.60Fr, 63.20.Kr, 71.20Nr.
Polythiophene (PT) and its derivatives [1–12] form an important class of organic conducting polymers for certain practical advantages. For example, these can be synthesized easily and can be doped with dopants [2–4], like ClO$_4^-$, AsF$_5$, NOPF$_6$ etc. These compounds are also chemically stable in air and moisture both in doped and undoped states. Ultraviolet photo-electron spectra (UPS) [3] of neutral polythiophene show existence of $\pi$-bands in the system and the Fermi energy, $E_F$ is $\sim$ 1 eV above the valence band (VB). So, neutral PT is an intrinsic semiconductor with a band gap of $\sim$ 2 eV between the valence band and conduction band (CB). However, metallicity can be induced in PT by doping. For example, high quality films of PT obtained by electro-chemical polymerization of dithiophene [2] under mild conditions exhibit a metallic transition with ClO$_4^-$ doping at $\sim$ 20 mol % doping level. The electrical conductivity of doped PT, however, shows wide variation depending on the method of preparation and dopants. UPS of PT films [4] also reveals a finite density of states at $E_F$ at saturation doping (30 mol % doping with ClO$_4^-$). Another important finding from UPS is the redshift [3,4] of $E_F$ by $\sim$ 0.8 eV at this doping. However, the mechanism for the insulator to metal transition in PT by doping is an open and polemical question.

Since the ground state of neutral PT is non-degenerate, dopants induce polaronic and bipolaronic defect states [8] in the system. At low doping concentrations, two optical transitions at $\sim$ 0.4 and $\sim$ 1.3 eV are due to polaronic defects states [5,8]. At intermediate doping level, these transitions are replaced by two other transitions [5,8] at $\sim$ 0.6 and $\sim$ 1.5 eV. These are bipolaronic transitions. Another interesting result is that X-ray photoelectron spectra (XPS) of C1s of PT [4] at saturation doping show an intense peak at $\sim$ 286 eV. This peak shows complete reversibility during doping and undoping cycle. So, this is an enhanced $\pi$ – $\pi^*$ shakeup satellite [4] arising from the modification of the electronic structure of PT films by doping. Furthermore, its intensity is not related to the dopant concentration (C) indicating the absence of localized positive charges in doped PT. This then implies that metallic conductivity in PT arises due to uniform extraction of $\pi$-electrons from PT by dopants. We further note that in high quality PT films [2], no inter-band optical transition is observed for C $\geq$ 20%.
Since one dimensional open chain polyenes can obtain stabilization from extensive bond alternation (Peierls’ instability [13]), formation of localized charges and a band gap between the VB and the bipolaron band, if formed should be the natural outcome. So, the absence of localized positive charges and the appearance of metallic conductivity in highly doped PT indicate that some other structural factor plays a significant role in the suppression of Peierls’ instability. This consideration leads us to explore the evolution of the electronic structure of cyclic polythiophenes upon doping. The motivation is that a planar mono-cyclic polyenes with \((4n + 2)\) \((n = 0,1, \ldots)\) \(\pi\)-electrons have innate aromatic stabilization [14]. On the other hand the same system with \(4n\) \(\pi\)-electrons are anti-aromatic. So, the innate aromatic stabilization of \((4n + 2)\) \(\pi\)-electrons ring can play fundamentally important role in the insulator to metal transition in doped PT. Other important considerations are that a ring has the desired translational invariance of the infinite system and its energy spectra is comparable to that of the infinite system.

In our model calculation we assume that PT ring can be treated as a planer conjugated polyene. The minimum number of thiophene units required to form a planer PT ring is twelve [12]. Electronic structures of undoped as well as doped PT rings are calculated within the framework of modified \(\sigma\)-bond compressibility model [14] which has been discussed thoroughly in Ref.9. The total Hamiltonian \((H)\) in this formalism is

\[
H = \sum_p \epsilon_p a_p^\dagger a_p + \frac{1}{2} \sum_{pq} (V_{pq} a_p^\dagger a_q + h.c.)
+ \frac{C'}{2} \sum_{pq} \sum V_{pq} (R_{pq} - R_{pq}^0 + B).
\]

Here, \(< pq >\) denotes summation over those atoms which are joined by a \(\sigma\) bond (nearest neighbor). In (1), \(a_p(a_p^\dagger)\) destroys (creates) an electron at the \(p\)-th site. \(\epsilon_p\), the self energy of the electron at the \(p\)-th site and the modified \(\sigma\)-bond compressibility model assume that

\[
\epsilon_p = \epsilon_p^0 - AX_p \sum_q [(R_{pq} - R_{pq}^0 + B)e^{-R_{pq}/B}
- (R_{pq}^0 - R_{pq}^0 + B)e^{-R_{pq}^0/B}] (2)
\]

Summation in (2) spans over all atoms bonded to the \(p\)-th atom. \(R_{pq}^0\) is the theoretical \(\sigma\)
bond length \[14\] of the \((p, q)\) bond. \(R_{pq}^{\text{ref}}\) denotes some suitably chosen reference bond length of the \((p, q)\) bond and the standard literature values \[6, 7, 9, 14\] of \(\sigma\) bond lengths in neutral PT are used for these parameters. \(\chi_p\) is the coupling parameter for the \(p\)-th site arising due to the coupling of the electronic structure to the lattice deformation. \(V_{p,q}\) is the tunneling matrix element that allows the electron at the \(p\)-th site to tunnel to the \(\sigma\)-bonded \(q\)-th site. We take \(V_{p,q} = -Ae^{-R_{p,q}/B}\), where \(A\) and \(B\) are the scaling parameters for the energy and the length respectively (ref. 14). The last term in \(H\) defines the elastic energy of the \((p, q)\) \(\sigma\) bond. Here \(C'\) is another adjustable parameter which we assume to be independent of the nature of the bonds.

The parameters \(\{\chi_p\}, \epsilon_p^0, A, B, C'\) are so chosen as to obtain the experimentally measured band gap \((E_g)\) between the VB and the CB in the neutral PT, the theoretically calculated valence band width and the ground state geometry of neutral PT which is comparable to the geometry obtained by other standard methods \[6–14\]. Values of these parameters are found to be identical to those obtained previously for PT chains in Ref.9, yielding a band gap of \(\sim 2\) eV and a valence band width of \(\sim 2.77\) eV. In addition, a single bipolaron defect creates two states at \(\sim 0.56\) and \(\sim 1.436\) eV above the VB. So, bipolaronic transitions also compare well with experimental values \[5, 7, 8\]. Furthermore, total +2 charge of the bipolaronic defect spreads over approximately ten thiophene units and 75% of the total charge resides over five units. So, for a single bipolaronic defect states, results do not depend significantly on the boundary condition.

Energy levels in neutral PT separate into five well defined bands. The lower-most and the uppermost levels in each band are non-degenerate while other levels in any given band are doubly degenerate. So, odd number \((2l-1, l=1,2,\ldots)\) of bipolarons can be introduced in PT ring by removing one pair of electrons from the uppermost level and the rest from the subsequent \((l-1)\) pairs of states and the configuration is unique. Since each thiophene unit has four \(\pi\)-electrons in its carbon backbone, the number of \(\pi\)-electrons in the polyene backbone of a PT ring containing \(N\) thiophene rings is \(4N\). But due to incorporation of \((2l-1)\) bipolarons, the polyene backbone in the doped system converts to a \([4(N-l) + 2]\) or \((4n+2)\)
π-electron system. On the other hand, for even number \((2l)\) of bipolarons, the number of π-electrons in the polyene backbone is \(4(N-l)\) or \(4n\). Furthermore, when a PT ring contains even number of bipolarons, the occupation of the last pair of degenerate levels can be either \((2,0)/(0,2)\) or \((1,1)\). In subsequent discussion these configurations will be referred to as \(S\) and \(T\) respectively.

The dependence of the gap between the highest occupied and the lowest unoccupied orbitals (HOMO and LUMO respectively) on \(C\) in a cyclic PT containing hundred thiophene units is shown in Fig.1. The evolution of the HOMO-LUMO gap in the open PT chain of same length is also included for comparison. We first discuss the case of odd bipolarons. While the periodicity in the open chain doped PT depends strongly on \(C\), for this case, the the unit cell of the doped system is found to be the thiophene ring as \(C\) increases beyond a critical value \((C \geq 14 \text{ mol%})\). The structure of the modified thiophene ring for some representative dopant concentrations above the critical value and also the structure of this ring in neutral PT are given in Fig.2. We note that the bond alternation in the polyene backbone of PT reduces significantly due to doping above the critical dopant concentration. So, we assume that if the bipolaronic doping creates a \((4n+2)\) π-electrons polyene backbone in PT, bands in the mother system undergo reorganization and a new CB ensues in the process. We further assume that energy levels in the new CB can be obtained from a Tight binding model with nearest neighbor hopping only. So, we write \(E(k) = (B/2) \cos k\) where \(B\) is the band width of the CB and as usual \(k = \frac{2\pi m}{N}\). Then for large \(N\) we obtain

\[
\Delta E = E_{\text{LUMO}}(N) - E_{\text{HOMO}}(N) \approx \frac{B\pi}{N} \sin k
\]

(3)

where \(k = \frac{(k_{\text{HOMO}} + k_{\text{LUMO}})}{2}\). We now consider two PT rings with \(N_1\) and \(N_2\) units respectively. These rings are doped with odd number of bipolarons but with same \(C\). From Eq.(3) we then obtain

\[
N_2 = \frac{\Delta E(N_1)}{\Delta E(N_2)} N_1
\]

(4)

Our results are given in Table I and the agreement is definitely excellent. We also show in Table I the Fermi energy, \(E_F\) \([-\left(\frac{E_{\text{HOMO}} + E_{\text{LUMO}}}}{2}\right]\) for two different values of \(N\) for a
given C and also for different C. It should be noted that $E_F$, particularly at higher dopant concentrations, does not show any appreciable dependence on N. This further shows the correctness of our hypothesis. The change of $E_F$, $\Delta E_F = |E_F(\text{doped}) - E_F(\text{neutral})|$ is shown in Fig.3. At $C = 30$ mol% we obtain $\Delta E_F \sim 0.84$ eV, while the experimental value [4] is $\sim 0.8$ eV. Hence, our theory also successfully predicts $\Delta E_F$.

We consider now the case of doping the system with even number of bipolarons. Since two uppermost degenerate levels are singly occupied in the T-configuration, the doped system cannot gain stabilization by pseudo Jahn-Teller effect [14]. So, the evolution of the structure of the T-configuration upon doping is similar to the case of doping PT with odd number of bipolarons. But due to the interaction of two polarons, the evolution of the HOMO-LUMO gap does not strictly follow Eq.(4). This can be seen by considering the case of 20 mol % dopant concentration. For $(N_1, N_2, N_3) = (80, 100, 120)$, we have $(\Delta E(N_1), \Delta E(N_2), \Delta E(N_3)) \simeq (0.0974, 0.0791, 0.0666)$. From the first two entries we obtain $N_2 \simeq 98.49$ while the last two entries yield $N_3 \simeq 118.76$. So, the deviation compared to the previous case is quite significant. The dependence of $\Delta E_F$ on C for a 100 unit PT ring is also shown in Fig.3. We note that the magnitude of $\Delta E_F$ for $C = 32$ mol % ($\sim 0.83$ eV) agrees very well with the experimental value [4].

The structure of the S-configuration at a given C is similar to the corresponding structure of the doped PT chain. This is the manifestation of pseudo Jahn-Teller effect. We further note that at $C = 20$ mol % and for $N = 100$ and 140 we obtain a gap of $\sim 0.55$ and $\sim 0.54$ eV respectively. Similarly, for $C = 40$ mol % we obtain $\sim 0.3$ eV for both cases. This shows that the HOMO-LUMO gap has reached the saturation value. So, the gain in electronic energy due to structural distortion has reached the asymptotic limit. The stabilization energy per unit cell ($\Delta E$) of the S-configuration over the other configuration is defined as $\Delta E_{ST} = \frac{(E_S - E_T)}{N}$. Its dependence on C and for two different values of N (100 and 140) are shown in Fig.4. It is important to note that $\Delta E_{ST}$ reduces with increasing N. For example, at $C = 20$ mol % and 40 mol %, the difference in $\Delta E_{ST}$ is $\sim -0.13$ and -0.18 respectively in the scale of $10^{-3}$ eV. Since we are considering values of N which are quite close, predictably
the difference is also small.

To understand the significance of our results we note that in a doped PT chain the unit cell contains more than one thiophene ring. So, the formation of a new CB upon doping is not possible and a transformation from the bipolaron lattice to the polaron lattice [8] has been proposed to explain the insulator-metal transition. On the other hand, the aromaticity of the polyene backbone of a cyclic PT doped with odd number of bipolarons drives the system towards the quinoid form. Since, the thiophene ring is again the unit cell in this structure, a new CB ensues in the doped system with \( E_F \) inside it. We further note that the theoretically estimated upper limit [14] of \( n \) beyond which a neutral cyclic polyene with \((4n+2)\pi\)-electrons would exhibit bond alternation is \( \sim 8 \). The experimental value [14], however, is \( \sim 4 \). On the other hand, values of \( n \) are at least an order of magnitude large in our calculations. So, we contend that our results for the case of odd number of bipolarons will not show any significant deviation due to further increase in \( N \).

For even number of bipolarons we find that the S-configuration is stable compared to the other configuration for values of \( N \) considered here. However, two important results, namely (i) the HOMO-LUMO gap has reached the asymptotic value, (ii) \( \Delta E_{ST} \) decreases with increasing \( N \), point to a \( N_c \), a critical value of \( N \) after which the T-configuration will be stable. Furthermore, for \( N \to \infty \), results cannot critically depend on the integer character of the number of bipolarons. So, we propose that the T-configuration will be the stable species for \( N > N_c \). Two important experimental results, namely the magnitude of \( \Delta E_F \) and the absence of inter-band transitions in heavily doped PT also indicate such possibility. We observe in this connection that the variation in the conductance of doped PT may be due to the presence of the T-configuration in the sample. So, we conclude that the evolution of the electronic structure of a cyclic PT upon doping can explain successfully many important experimental results including the metal-insulator transition.
REFERENCES

[1] A. J. Heeger, S. Kivelson, J. R. Schrieffer and W. P. Su, Rev. Mod. Phys. 60, 781 (1988).

[2] T. -C. Chung, J. H. Kaufman, A. J. Heegar, and F. Wudl, Phys. Rev. B 30, 702 (1984).

[3] M. Logdlund, R. Lazzaroni, S. Stafstrom, W. R. Salaneck, and J. -L. Bredas, Phys. Rev. Lett. 63, 1841 (1989).

[4] Y. Jugnet, G. Tourillon, and T. M. Duc, phys. Rev. Lett. 56, 1862 (1986).

[5] G. Horowitz, A. Yassar, and H. J. von Bardeleben, Synth. Met. 62, 245 (1994).

[6] F. C. Lavarda, M. C. dos Santos, D. S. Galvao, B. Laks, Phys. Rev. B 49, 979 (1994).

[7] J. L. Bredas, B. Themans, J. G. Fripiat, J. M. Andre and R. R. Chance, Phys. Rev. B 29, 6761 (1984).

[8] S. Stafstrom and J. -L. Bredas, Phys. Rev. B 38, 4180 (1988).

[9] D. Giri, and K. Kundu, Phys. Rev. B 53 (1996).

[10] Ch. Ehrendorfer and A. Karpfen, J. Phys. Chem. 98, 7492 (1994).

[11] J. Cornil, D. Beljonne and J. L. Bredas, J. Chem Phys. 103, 842 (1995).

[12] A. J. W. Tol, Synth. Met. 74, 95 (1995).

[13] R. E. Peierls, Quantum Theory of Solids (Oxford University Press, 1974).

[14] L. Salem, The Molecular Orbital Theory of Conjugated Systems (Benjamin, New York, 1966).
FIGURES

FIG. 1. The HOMO-LUMO gap (in eV) as a function of mol % dopant concentration: (a) for odd number of bipolarons in a PT ring (○); (b) for T-configuration (□); (c) for S-configuration (+), (d) for open PT chain (×).

FIG. 2. The bond lengths (in Å) of the thiophene ring at different dopant concentration: (a) at 18 mol %; (b) 26 mol %; (c) 30 mol %; (d) 50 mol %. Values within the parenthesis are for neutral PT ring.

FIG. 3. $\Delta E_F$ (in eV) as a function of dopant concentration (mol %):(a) for odd number of bipolarons (□); (b) for T-configuration (+).

FIG. 4. $\Delta E_{ST}$ (in eV) as a function of dopant concentration (mol %):(a) for 100 unit PT ring (□); (b) for 140 unit PT ring (+).
TABLES

TABLE I. Calculated values of $N_2$ at different dopant concentrations (mol %). Values of $E_F$ and $B$ (in eV) at different N and also at different C.

| % Defect | N$_1$ | $\Delta E(N_1)$ | N$_2$ | $\Delta E(N_2)$ | $N_2$ (calculated) | $E_F(N_1)$ | $E_F(N_2)$ | $B(N_1)$ | $B(N_2)$ |
|----------|------|----------------|------|----------------|------------------|------------|------------|---------|---------|
| 15       | 91   | 0.06838        | 117  | 0.05322        | 116.924          | -0.6554    | -0.6549    | 3.2336  | 3.2334  |
| 20       | 90   | 0.09245        | 110  | 0.07566        | 109.967          | -0.6344    | -0.6342    | 3.3967  | 3.3965  |
| 25       | 88   | 0.11161        | 120  | 0.08186        | 119.979          | -0.6743    | -0.6741    | 3.5459  | 3.5456  |
| 30       | 100  | 0.10522        | 140  | 0.07516        | 139.992          | -0.7638    | -0.7637    | 3.6492  | 3.6491  |
| 40       | 95   | -0.11549       | 125  | 0.08777        | 124.998          | -1.0015    | -1.0015    | 3.7682  | 3.7682  |
| 50       | 100  | 0.11084        | 140  | 0.07917        | 139.999          | -1.2629    | -1.2629    | 3.8360  | 3.8360  |