Electronic Structure of Thiophene Oligomer Dications: An Alternative Interpretation from the Spin-Unrestricted DFT Study

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The geometric and electronic structures of oligothiophene dications (with 6 to 12 monomers) have been revisited using the spin-unrestricted broken symmetry hybrid density functional B3LYP method. It is found that there exists a transition region of bipolaron to two-polaron structure conversion in the moderately sized oligomers, as that had been reported earlier in an AM1-CI calculation. According to our calculation, the transition region should be from hexamer to octamer. TD-DFT simulation led to a different rationalization of the experimental UV/visible spectra, which suggested the coexistence of bipolaron and two-polaron state in the transition region.

1. Introduction

The thorough understanding of the properties of the cation and dication of organic oligomers is a fundamental step toward the understanding of the electric conductivity of the doped conjugated organic polymers.[1−3] For example, people paid much attention to the study of the thiophene oligomers in order to probe the mechanism of the conductivity for the charg-doped polythiophene. Unfortunately, whether it has a spinless polarons structure (radical) or bipolaron (nonradical) structure in high-doped polythiophenes is still being debated.[4−6]

The high-charge-doped polythiophene had been regarded as a bipolaron structure for a long time. The two electronic adsorption bands in UV/visible/near-infra spectra and the ESR nonactivity had seemed to strongly support this judgment.[7−9] Most early theoretical computations had been focused on the bipolaron electronic state.[10−14] However, there existed some inconsistencies between the experimental and theoretical expectations. For example, according to the FBC model, if the bipolaron structure were the dominant structure, the second transition should have been far less intense, which is contradictory to the similar intensities of both bands in UV/visible absorption spectra.[15,16]

Owing to the above inconsistency, more recent works tended to accept the polaron structure as the dominant structure in polythiophene. The doubly oxidized sexithiophene ($6T^{2+}$), which was regarded as the bipolaron structure, showed only one strong absorption band, unlike what happened in charge-doped polythiophenes, where two similar intensity bands were observed. Meanwhile, two strong absorption bands were observed in the singly oxidized sexithiophene ($6T^{+}$). Thus Furukawa et al. concluded that the charge defects of the doped polythiophenes were more likely polarons rather than bipolarons.[16,17] Furthermore, van Haare et al. carefully compared the optical properties of 6T, 9T, and 12T in the oxidized processes and concluded that two separate polarons instead of one bipolaron more likely existed in the thiophene oligomer dications, when the monomer number was up to twelve.[4,18] The most recent evidence supporting the above arguments was an experiment using cyclic voltammetry and variable-temperature UV/visible/near-IR spectroscopy made by Apperloo et al.[19]

At the same time, the ESR nonactivity was interpreted by the assumption of the interchain polaron dimerization, which was called the “pi-dimer”.[20,21] It was also regarded as the origin of the electric conductivity.[22] A detailed interpretation could be found in a very recent work by Beljonne et al.[23]

The semiempirical AM1-CI calculations done by Tol on the stability of the two-polaron state over the bipolaron state confirmed that there should exist a transition region in oligothiophenes; when the oligomers are longer, the two-polaron state should be more stable, while the shorter oligomers prefer the bipolaron state. He predicted this transition crossover to be at the dodecamer after taking into consideration both theoretical and experimental facts.[24,25] However, when the counterions were taken into account, such as in the works of Irle et al.,[26−28] who employed the TCSCF and spin-unrestricted DFT to investigate the bipolaron to two-polaron transitions, reversed conclusions were reached surprisingly.

Actually, the dispute has not come to an end. Some more recent experimental and theoretical works still claimed that the bipolaron structure was likely the main species in doped polythiophenes.[29,30] For example, Silva employed the SSH model combined the Pariser−Parr−Pople model and Brazovskii-Kirova symmetry breaking interaction to find that the bipolaron state is more stable than the polaron state at low doping.[30] Thus, more experimental and theoretical work should be done before setting an end to this dispute.

This work presented a DFT calculation on the geometric and electronic properties of the thiophene oligomer dications. The spin-restricted and spin-unrestricted ground states of nT^{2+} (n is from 2 to 12) were computed simultaneously, to make it clear whether the polaron or the bipolaron structure is more likely the dominant structure in the oligomers. The electronic absorption bands of $6T^{2+}$, $9T^{2+}$, and $12T^{2+}$ were also evaluated using the TD-DFT method, which were compared with experimental results.

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2. Computational Method

It is known that the broken-symmetry solutions often have lower energies than the corresponding symmetrical solutions for the lowest singlet state of radicals.[34-38] For the broken-symmetry method, the HOMO and LUMO orbitals are mixed to destroy the $\alpha \sim \beta$ spatial symmetry in the initial guess of the molecular orbitals. In our work, both the spin-restricted (close-shell) and the spin-unrestricted broken-symmetry (open-shell) DFT method were employed to get corresponding optimal geometries and electronic structures.

Very accurate calculation of electronic transitions for open-shell species is a difficult job. Time-dependent density functional theory (TD-DFT) had been shown very efficient in calculating the electron transitions for a variety of molecular species.[39] Because of the spin contamination problem in spin-unrestricted computation, its application to open-shell species was very uncommon. However, some more recent works showed that this method could also give results in good agreement with the electronic absorption spectra.[40,41] Thus we would try to apply the TD procedure on the optimized structures for both the open-shell and the close-shell state of nT^{2+} ($n = 6, 9, 12$). It could be seen that the coincidence between the computational and experimental results is very encouraging.

All the computations were carried out with the hybrid density functional method B3LYP using the Gaussian 98 package;[42] the geometry optimization and the electronic properties calculation were all done at the basis set of 6-31G*.

3. Results and Discussion

All the structures of the dications $[\mathrm{H}-(\mathrm{C_4H_2S})_n-\mathrm{H}]^{2+}$, denoted as nT^{2+}, for n equals 2 to 12, were optimized with two constraints: only the all-anti conformations were treated, and the structures were kept planar.

It was found that for short oligomers up to 5T^{2+}, spin-restricted wave functions were stable, which means that small oligomer dications should exist in a bipolaron form. This conclusion is in accordance with the common view that the bipolarons exist in the short oligothiophene;[43,44] however, for 6T^{2+} and longer oligomers, the restricted ground state becomes unstable, and the unrestricted singlet ground state turns out to be stable. This transformation will be analyzed in detail in the following sections. For simplicity, we illustrate only the situation of even number oligomers below.

3.1. Ground-State Energy. When the monomer number is less than six, the spin-restricted and spin-unrestricted methods actually result in the same ground state. Afterward, the energy difference between the two methods appears and goes up gradually as n increases, which implies that the two-polaron structure becomes more and more stable than the bipolaron structure as the oligomer length increases. For 6T^{2+}, this energy difference ($\Delta E = E(\text{bipolaron}) - E(\text{polaron})$) is only around 0.18 kcal/mol. When the monomer number increases to nine, it increases to 3.08 kcal/mol. While the number is up to twelve, this difference is as large as 4.24 kcal/mol, and the difference does not show any evidence of convergence at that length. It implies that the bipolaron structure would be the energetically preferred structure in the short oligomers, and there might be a bipolaron to two-polaron state transition when the monomer number increases. In this respect, our result is coincident to the AM1-CI calculation of Tol.[25] But it seems that the semiempirical calculation overestimated the energy difference; for example, our calculation showed that ΔE is 1.62 kcal/mol for the octamer and 3.2 kcal/mol for the decamer, compared to around 5 kcal/mol and 10 kcal/mol, respectively, from AM1-CI calculation (estimate from Figure 1 in ref 25). According to our calculation, the bipolaron state to two-polaron state transition region might be extended from the hexamer to the octamer. Further discussion based on the electronic transition computation will be given in Section 3.4.

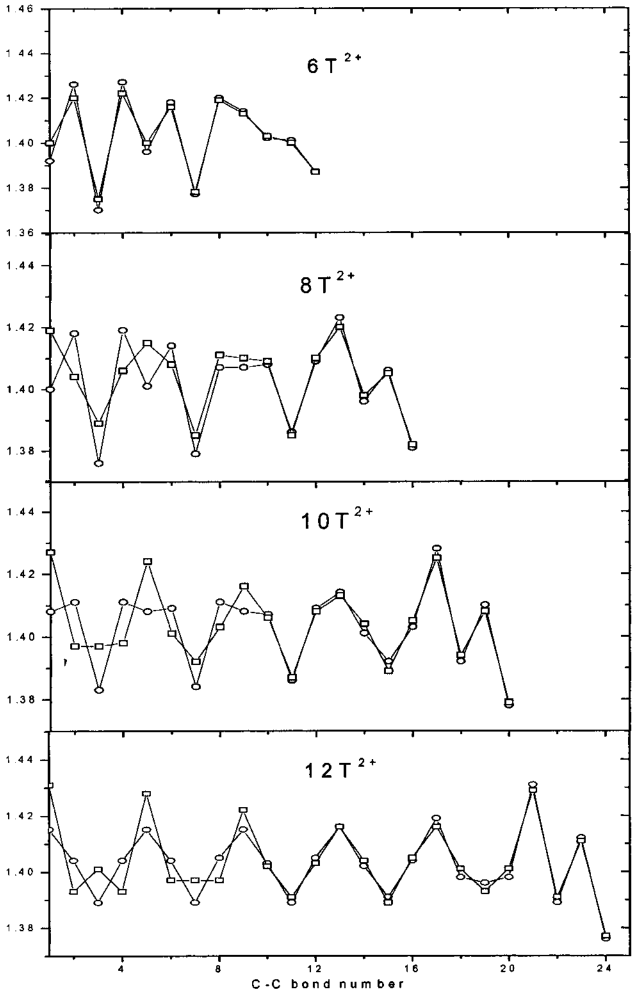

Figure 1. The bond length (Å) versus the C−C bond number of the right half of the nT^{2+} ($n = 6, 8, 10$, and 12) at RB3LYP/6-31G* (○) and UB3LYP/6-31G* (□) levels.

3.2. Geometry. The spin-restricted state geometries and other properties of the dications had been elucidated earlier using semiempirical methods (AM1, PM3), ab inito SCF methods and pure DFT methods.[43-46] In our calculations, the geometries of this state are coincident with those obtained by the pure DFT methods BLYP.[46]

The computed lengths of successive C−C bonds in the conjugated π system of the oligomers nT^{2+} ($n = 6, 8, 10$, and 12), which were optimized using the B3LYP method, are shown in Figure 1. It could be found that the spin-restricted and spin-unrestricted ground-state geometries showed different trends when the monomer number increases. The most significant change is in the central-most inter-ring C−C bond. For 6T^{2+}, this bond length (1.400 Å) of the spin-unrestricted state is slightly longer than that of the restricted state (1.392 Å), both of which have shown double-bond property obviously. As the monomer number increases, the central-most inter-ring C−C bond length of the spin-unrestricted state quickly becomes longer than the neighboring inner-ring C−C bond length, while the spin-restricted state does not show this trend. For four thiophene rings in the center of a 12T^{2+} chain, the average inter-ring C−C bond length is 1.429 Å and 1.415 Å from the unrestricted and

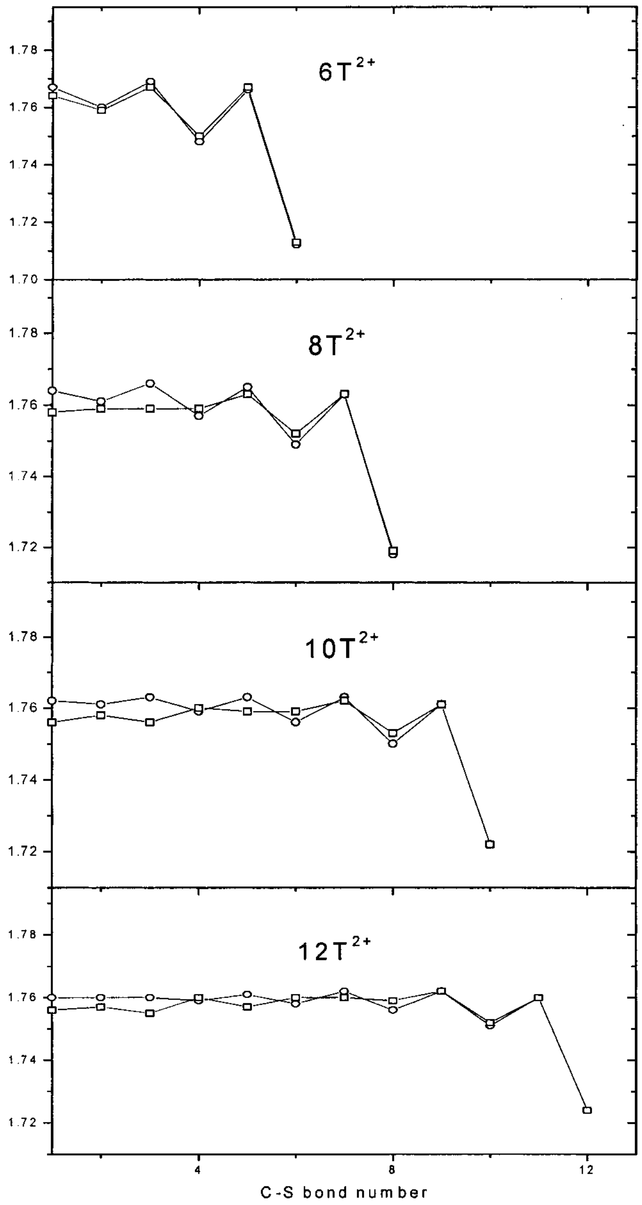

Figure 2. The bond length (Å) versus the C−S bond number of the right half of the nT^{2+} (n = 6, 8, 10, and 12) at RB3LYP/6-31G* (○) and UB3LYP/6-31G* (□) levels.

restricted B3LYP calculations, respectively. The average inner-ring C−C and C=C bond length is 1.399 Å and 1.395 Å from UB3LYP calculation and 1.389 Å and 1.404 Å from RB3LYP calculation, respectively. The central four rings of the unrestricted state of 12T^{2+} show some marked benzenoid property, while those of the restricted state do not. Meanwhile we noticed that the central C−C bond length increased to 1.431 Å in the UB3LYP calculation, which is transformed into a single bond from the double bond. This situation indicates that the longer doubly oxidized oligothiophene chain is divided into two separate parts with the quinoid structure, each of which possesses one polaron. These two parts are separated by the benzenoid thiophene rings in the middle of the chain. For this reason, the spin-unrestricted state is called the "two-polaron state", corresponding to the "bipolaron state" for the restricted state.

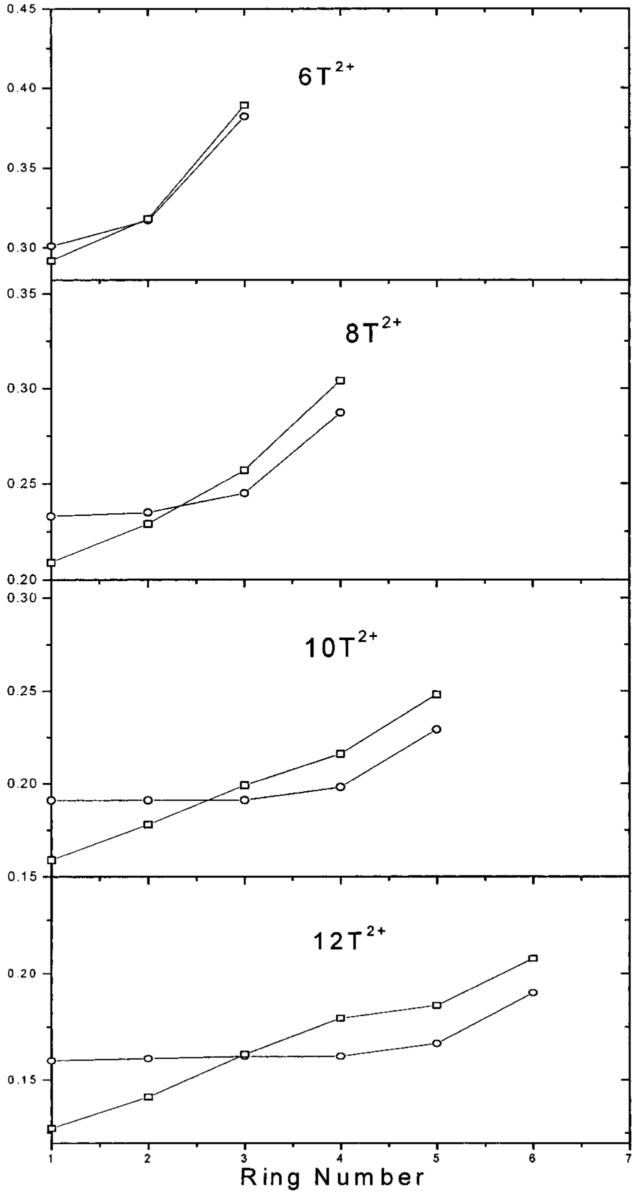

Figure 3. Charge per ring profile for half the nT^{2+} (n = 6, 8, k10, and 12) at RB3LYP/6-31G* (○) and UB3LYP/6-31G* (□) levels.

The evolution of the C−S bond lengths in the series nT^{2+} oligomers are shown in Figure 2. Experimental investigation had shown that C−S bond lengths in poly(3-methyl-thiophene) does not change upon doping.[47] Our calculation proved that such inflexibility is possible. The C−S bond length converged in the central part of these oligomers for both methods (for neutral 12T, it converged to 1.758 Å; for 12T^{2+}, 1.76 Å in the spin-restricted state and 1.757 Å in the spin-unrestricted state). However, there still exists one obvious discrepancy; from Figure 2, one could easily find that the trend of the bond length variation in the spin-restricted state is the reverse of that of the spin-unrestricted state in the centra-most four rings.

3.3. Charge Distribution. In this section, the conventional Mulliken population analysis method was adopted to calculate the total net charges per thiophene ring. The results were illustrated in Figure 3. In the spin-restricted state, except for the largest positive charges of the two outer rings, the inner rings have almost equal charges, which means that the doped-charges distribute averagely in the whole chain. On the other hand, in the spin-unrestricted state, the charge per ring reduced gradually from the end to the middle of the chain. Since the spin-unrestricted state is the dominant structure in long oligomers, this property indicated that the two polarons tend to exist separately near the two ends of the chain, while the rings in the middle are more or less like the structure in neutral species. It

TABLE 1: Calculated and Observed Electronic Transitions (eV) for Doubly Oxidized Oligothiophenes

oligomer	TD-RB3LYP/6-31G*[a]	TD-UB3LYP/6-31G*	observed[b]
$6T^{2+}$		1.31 (0.2238)	
	1.58 (2.6113)	1.54 (1.8110)	1.28
		1.87 (0.5250)	1.42
	2.76 (0.1907)	2.81 (0.1317)	2.35
$9T^{2+}$	1.02 (3.4590)	0.95 (2.0368)	0.82
		1.13 (0.1356)	0.95
	2.32 (0.7669)	1.66 (1.5028)	1.59
		1.85 (0.3868)	
$12T^{2+}$	0.77 (4.1933)	0.75 (2.4764)	0.88
	1.94 (1.3728)	1.60 (2.7085)	1.75

[a] Oscillator strength in parentheses. [b] Ref 18.

can be found that our result is different from the AM1-CI calculation in the charge values in the middle of the chain. For example, for the two-polaron state of decamer, the DFT shows that the lowest charge of the inner rings is 0.16 and the highest charge of the end rings is 0.25, while the AM1 shows that the lowest charge of the inner rings is 0.06 and the highest charge of the next end rings is 0.29.[25] Even at the dodecamer level, the central-most ring still has some charges; the DFT calculation implies that the two polarons are not entirely independent of each other.

3.4. The Electronic Transitions. The time-dependent DFT calculation of the electronic absorption spectra of the oligothiophene dications is tabulated in Table 1. It can be found that the number and the locations of the absorption peaks of the spin-unrestricted state are very close to the observed spectra.[16−18,48]

The TD calculation showed that the closed-shell (bipolaron) $6T^{2+}$ has one strong absorption peak at 1.58 eV and a very weak absorption peak at 2.76 eV. It is in good agreement with the experiment that there are two obvious absorption peaks in 1.28 eV and 2.35 eV, except for a “minor” inconsistency, a shoulder at 1.42 eV had always been found in the experimental observed.[16−18,48] This “shoulder” was attributed to the vibrational coupling. Accordingly, $6T^{2+}$ was classified as a bipolaron. However, for $6T^{2+}$, the ground-state energy difference of the spin-unrestricted and the spin-restricted state is very small, and it is reasonable to assume that these two species exist simultaneously. Here we would like to suggest a different interpretation of the spectra. Let us concentrate on the open-shell (two polarons) $6T^{2+}$. There exist more absorption peaks, the strongest peak is at 1.54 eV, and the quite strong peak is at 1.87 eV, while the other two weak peaks are at 1.31 eV and 2.81 eV. When we added both spectra (closed-shell and open-shell) into a new one in Figure 4, which was obtained by a convolution of the calculated transition energies with 0.5 eV full widths at half-maximum Gaussian function, the spectra showed the strongest absorption band appeared at around 1.56 eV, with a shoulder at 1.87 eV, and a weak absorption peak at 2.80 eV, i.e., the shoulder is not contributed from the vibrational coupling, but from the second electronic absorption band of the two-polaron structure.

For $9T^{2+}$, besides the one strong absorption band with a shoulder found at around 0.9 eV, van Haare et al. found another weak band at 1.59 eV,[13] which was ignored by Apperloo et al. in another experiment.[14] Here we give a detailed analysis on this problem. In the two-polaron state, two absorption bands were found: one is a strong peak at 0.95 eV with a shoulder at 1.12 eV, the other is a weaker peak at about 1.70 eV. The latter is composed of two absorption bands with the stronger peak at 1.66 eV and the much weaker peak at 1.85 eV. In the bipolaron state, two bands were calculated to be at 1.02 and 2.32 eV, respectively. The observed spectrum, which is composed of one band at 0.82 eV with a shoulder at 0.95 eV and another band at 1.59 eV, seems more likely attributed to the two-polaron state.[18] We also calculated the absorption spectra of $9T^{+}$ and found a strong absorption at 1.47 eV with a shoulder at 1.55 eV, very close to the second absorption band of $9T^{2+}$. That might be the reason the second band was ignored in Apperloo’s stepwise oxidization.[19]

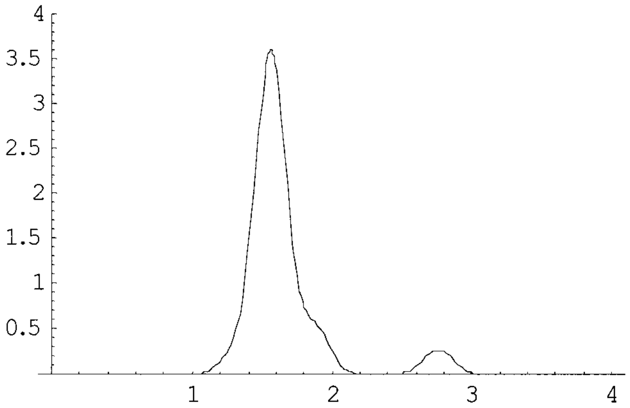

Figure 4. The TDDFT absorption spectra of $6T^{2+}$, composed of the open-shell and closed-shell state with same proportion. The peak is a convolution of the calculated transition energies with 0.5 eV full width at half-maxium Gaussian function.

When the number of thiophene rings increases to twelve, we found two strong bands with similar intensity at 0.71 eV and 1.56 eV in the two-polaron state, compared to the one strong band at 0.77 eV and one weaker band at 1.94 eV in the bipolaron state. According to the experimental results that $12T^{2+}$ has two absorption bands of similar intensity at 0.75 eV and 1.60 eV, the two-polaron state should be more reasonable.[18]

4. Summary and Conclusion

In this paper, we use the hybrid DFT method B3LYP to revisit the structures of the doubly oxidized oligothiophenes. It is found that the closed-shell bipolaron should be the primary ground state for the short oligothiophenes, which is in agreement with the experimental results performed earlier. While the number of the monomer increases, the open-shell two-polaron state will be more stable, replacing the close-shell structure, and gradually becomes the dominant state. Comparing the previous conclusion that the transition crossover happens at the dodecamer,[18,25] our computational results of energy values shorten the transition region predicted and find that the bipolaron state and two-polaron state may coexist from the hexamer to octamer. When the ring number increases, the two-polaron state becomes dominant. Our calculated absorption bands are in good agreement with the experimental spectra. Thus the quinonoid structure that has been widely accepted exists only in the limited length oligomers dications and disappears in the longer oligothiophenes dications, or charge-doped polythiophene.

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References and Notes

(1) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
(2) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(3) *Conjugated Polymers: The Novel Science and Technology of Highly Conjugated and Nonlinear Optically Active Material*; Brédas, J. L., Silbey R., Eds.; Kluwer Academic Publishing: The Netherlands, 1991.

(4) Salaneck, W. R.; Friend, R. H.; Brédas, J. L. *Phys. Rep.* **1999**, *319*, 231.

(5) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.

(6) Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 1013.

(7) Kaneto, K.; Hayashi, S.; Ura, S.; Yoshino, K. *J. Phys. Soc. Jpn.* **1985**, *54*, 1146.

(8) Chen, J.; Heeger, A. J.; Wudl, F. *Solid. State Commun.* **1986**, *58*, 251.

(9) Fichou, D.; Horowitz, G.; Xu, B.; Gamier, F. *Synth. Met.* **1990**, *39*, 243.

(10) Brédas, J. L.; Thémans, B.; Fripiat, J. G.; André, J. M.; Chance, R. R. *Phys. Rev.* **1984**, *B29*, 6761.

(11) Lazzaroni, R.; Rachidi, S.; Brédas, J. L. *Science and Applications of Conducting Polymers*; Salaneck, W. R., Clark, D. T., Samuelsen, E. J., Eds.; Adam Hilger: Bristol, 1991.

(12) Stafstrom, S.; Brédas, J. L. *Phys. Rev.* **1988**, *B38*, 4180.

(13) Brédas, J. L.; Wudl, F.; Heeger, A. *J. Solid State Commun.* **1987**, *63*, 577.

(14) Bertho, D.; Jouanin, C. *Phys. Rev.* **1987**, *B35*, 626.

(15) Fesser, K.; Bishop, A. R.; Campbell, D. K. *Phys. Rev. B.* **1983**, *27*, 4804.

(16) Furukawa, Y. *J. Phys. Chem.* **1996**, *100*, 15644.

(17) Yodonuma, N.; Furukawa, Y.; Tasumi, M.; Kuroda, M.; Nadayama, J. *Chem. Phys. Lett.* **1996**, *255*, 431.

(18) van Haare, J. A. E. H.; Havinga, E. E.; van Dongen, J. L. J.; Janssen, R. A. J.; Cornil, J.; Brédas, J. L. *Chem. Eur. J.* **1998**, *4*, 1509.

(19) Apperloo, J. J.; Janssen, R. A. J.; Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 7042.

(20) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.

(21) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J.-F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.

(22) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P. T.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.

(23) Beljonne, D.; Cornil, J.; Sirringhaus, H.; Brown, P. J.; Shkunov, M.; Friend, R. H.; Brédas, J. L. *Adv. Funct. Mater.* **2001**, *11*, 229.

(24) Tol, A. J. W. *Synth. Met.* **1995**, *74*, 95.

(25) Tol, A. J. W. *Chem. Phys.* **1996**, *208*, 73.

(26) Irle, S.; Lischka, H. *J. Chem. Phys.* **1995**, *103*, 1508.

(27) Irle, S.; Lischka, H.; Eichkorn K.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, *257*, 592.

(28) Irle, S.; Lischka, H. *J. Chem. Phys.* **1997**, *107*, 3021.

(29) Harima, Y.; Eguchi, T.; Yamashita, K.; Kojima, K.; Shiotani, M. *Synth. Met.* **1999**, *105*, 121.

(30) Silva, G. M. E. *Phys. Rev. B* **2000**, *61*, 10777.

(31) Chen, J.; Heeger, A. J.; Wudl, F. *Solid State Commun.* **1986**, *58*, 281.

(32) Kahol, P. K.; Clark, W. G.; Mehring, M. *Conjugated Conducting Polymers*; Kiess, H., Ed.; Springer-Verlag: Berlin, 1992.

(33) Kivelson, S.; Heeger, A. J. *Phys. Rev. Lett.* **1985**, *55*, 308.

(34) Mitani, M.; Mori, H.; Takano, Y.; Yamaki, D.; Yoshioka, Y.; Yamaguchi, K. *J. Chem. Phys.* **2000**, *113*, 4035.

(35) Mitani, M.; Yamaki, D.; Takano, Y.; Kitagawa, Y.; Yoshioka, Y.; Yamaguchi, K. *J. Chem. Phys.* **2000**, *113*, 10486.

(36) Mitani, M.; Takano, Y.; Yoshioka, Y.; Yamaguchi, K. *J. Chem. Phys.* **1999**, *111*, 1309.

(37) Mitani, M.; Yamaki, D.; Yoshioka, Y.; Yamaguchi, K. *J. Chem. Phys.* **1999**, *111*, 2283.

(38) Lahti, P. M.; Ichimura, A. S.; Sanborn, J. A. *J. Phys. Chem. A* **2001**, *105*, 251.

(39) Koch, W.; Holthausen, M. C.; A Chemist's Guide to Density Functional Theory; Wiley-VCH: Weinheim, Germany, 2000.

(40) Radziszewski, J. G.; Gil, M.; Gorski, A.; Spanget-Larsen, J.; Waluk, J.; Mróz, B. J. *J. Chem. Phys.* **2001**, 115, December.

(41) Chatgilialoglu, C.; Ferreri, C.; Bazzanini, R.; Guerra, M.; Choi, S.-Y.; Emanuel, C. J.; Horner, J. H.; Newcomb, M. *J. Am. Chem. Soc.* **2000**, *122*, 9525.

(42) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(43) Alemán, C.; Julià, L. *J. Phys. Chem.* **1996**, *100*, 14661.

(44) (a) Ehrendorfer, Ch.; Karpfen, A. *J. Phys. Chem.* **1994**, *98*, 7492. (b) Ehrendorfer, Ch.; Karpfen, A. *J. Phys. Chem.* **1995**, *99*, 5341.

(45) Cornil, J.; Beljonne, D.; Brédas, J. L. *J. Chem. Phys.* **1995**, 103, 842.

(46) Moro, G.; Scalmani, G.; Cosentino, U.; Pitea, D. *Synth. Met.* **1998**, 92, 69.

(47) Tourillon, G.; Flank, A. M.; Lagarde, P. *J. Phys. Chem.* **1988**, *92*, 4397.

(48) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Hutterlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.