Small Band-Gap Polymers: Quantum-Chemical Study of Electronic Structures of Degenerate π-Conjugated Systems

Sung Y. Hong* and Kyong W. Lee

Department of Chemistry, Institute of Natural Science, Kosin University, Pusan 606−701, South Korea

Received August 9, 1999. Revised Manuscript Received October 12, 1999

In search of stable and small band-gap polymers, we have quantum-chemically investigated the electronic structures of various polypentafulvalenes (PFVs), which are degenerate or nearly degenerate in the ground state. Geometrical parameters of the polymers were optimized through semiempirical Hartree−Fock band calculations at the Austin model 1 (AM1) level. Electronic structures of the polymers were obtained through modified extended Hückel band calculations by adopting AM1-optimized geometries. In comparison with *trans*-polyacetylene (*t*-PA), PFV was estimated to possess a small band gap (corresponding to $\lambda_{\max}$) of 1.13 eV and a high oxidation potential, even though the polymeric chain exhibits a bond-length alternation whose value is similar to that of *t*-PA. These results come from the strong bonding interactions between the frontier orbitals of the *t*-PA-like backbone and the π^* orbitals of the vinylene fragments. It is found that methoxy substitution at C5 and C5′ decreases the band gap by 0.38 eV, whereas the substitution at C4 and C4′ increases the band gap by 0.26 eV. In cyano-substituted PFVs, the trend is reversed. Fusion with vinylene−X fragments (X = O, S, NH) does not significantly affect the band gap of PFV but decreases the oxidation potential. We explained the effect of electron-donating and -accepting substituents and fusion of the vinylene−X fragments on the electronic properties of PFV through molecular orbital arguments.

Introduction

During the past decade, a great deal of experimental and theoretical effort has been devoted to the design of very small band-gap polymers, which would exhibit intrinsic electrical conductivity without the help of dopants or at least semiconductive properties in the ground states. Owing to their relatively good environmental stability and small band gaps, heterocyclic polymers have been chosen as major target materials for structural modification to achieve such a goal.[1−9] The strategy of modification toward a quinonoid structure is based on the work of Brédas,[10] which showed that the band gap of an aromatic system decreases as the quinonoid character of the backbone increases. Polyisothianaphthene (PITN) and poly(thienylene methines) were reported to exhibit small band gaps below 1 eV.[1,2] However, it has been suspected that these polymers were of doped states.[11,12] Theoretical calculations[13−15] and spectroscopic investigations[15,16] have demonstrated that PITN in the ground state is of the quinonoid form. Chandrasekhar et al. reported through a spectroelectrochemical investigation[11] that PITN exhibited an absorption peak at 633 nm (2.0 eV) in the neutral state and at 830 nm (1.5 eV) in the electrochemically doped state. Different calculation methods predicted different band gaps for quinonoid PITN: the extended Hückel (EH; 0.8 and 1.16 eV),[13,14] the valence effective Hamiltonian (VEH; 1.19 eV),[15] and the modified extended Hückel (MEH; 2.28 eV) methods.[17] Poly(heteroarylene methines) have been consistently supported by theoretical calculations to possess small band gaps, because the effects of heteroatoms and C1−C4 interactions on the band gap become negligible due to their alternating

---

* E-mail: shong@sdg.kosin.ac.kr. Fax: +82 51 405 9760.

(1) Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. *J. Chem. Phys.* **1985**, *82*, 5717.

(2) Jenekhe, S. A. *Nature* **1986**, *322*, 345.

(3) Bräunling, H.; Blöchl, G.; Becker, R. *Synth. Met.* **1991**, *41−43*, 487.

(4) Bräunling, H.; Blöchl, G.; Becker, R. *Synth. Met.* **1991**, *41−43*, 1539.

(5) Hanack, M.; Mangold, K.-M.; Röhrig, U.; Maichle-Mössmer, C. *Synth. Met.* **1993**, *60*, 199.

(6) Lorcy, D.; Cava, M. P. *Adv. Mater.* **1992**, *4*, 562.

(7) Tamao, K.; Yamaguchi, S.; Ito, Y.; Matsuzaki, Y.; Yamabe, T.; Fukushima, M.; Moris, S. *Macromolecules* **1995**, *28*, 866.

(8) Ferraris, J. P.; Lambert, T. L. *J. Chem. Soc. Chem. Commun.* **1991**, 1268.

(9) Zotti, G.; Schiavon, G.; Berlin, A.; Fontana, G.; Pagani, G. *Macromolecules* **1994**, *27*, 1938.

(10) Brédas, J. L. *J. Chem. Phys.* **1985**, *82*, 3808.

(11) Chandrasekhar, P.; Masulaitis, A. M.; Gumbs, R. W. *Synth. Met.* **1990**, *36*, 303.

(12) Patil, A. O.; Wudl, F. *Macromolecules* **1988**, *19*, 2663.

(13) Lee, Y.-S.; Kertesz, M. *J. Chem. Phys.* **1988**, *88*, 2609.

(14) Nayak, K.; Marynick, D. S. *Macromolecules* **1990**, *23*, 2237.

(15) Hoogmartens, I.; Adriaensens, P.; Vanderzande, D.; Gelan, J.; Quattrocchi, C.; Lazzaroni, R.; Brédas, J. L. *Macromolecules* **1992**, *25*, 7347.

(16) Wallnöfer, W.; Faulques, E.; Kuzmany, H.; Eichinger, K. *Synth. Met.* **1989**, *28*, C533. Hoogmartens, I.; Vanderzande, D.; Martens, H.; Gelan, J. *Synth. Met.* **1991**, *41−43*, 513. Kiebooms, R.; Hoogmartens, I.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Macromolecules* **1995**, *28*, 4961.

(17) Hong, S. Y.; Marynick, D. S. *J. Chem. Phys.* **1992**, *96*, 5497.

10.1021/cm990496n CCC: $19.00

aromatic and quinonoid sequences.[18−20] Nonetheless, a variety of poly(heteroarylene methines), experimentally prepared, have demonstrated poor conductivities and absorption peaks near 2 eV.[3−5,21,22] These phenomena have been ascribed to the possibilities of short chain lengths, nonplanar conformations, and defects by a large amount of sp^3 C atoms. Copolymers of two different types of cyclic units, whose homopolymers exhibit different isomeric structures in the ground state, have been investigated as candidate materials for providing small band gaps.[6,23−27] Poly(isothianaphthene bithiophene) was reported to show an absorption edge near 1.58 eV, with a peak at 2.12 eV.[6] Yamashita et al. synthesized a copolymer consisting of two thiophene rings and one benzo[1,2-c;3,4-c′]bis[1,2,5]thiadiazole ring in a unit cell.[26] This copolymer in the ground state was reported to display a band edge at 0.5 eV and an absorption peak at about 1.0 eV.

Because heterocyclic conjugated polymers such as polythiophene are nondegenerate in the ground state, two isomers are possible: aromatic and quinonoid forms whose electronic structures are different from each other. It has usually been observed that when the aromatic form transforms into the quinonoid form, the highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) are reversed.[28,29] Therefore, by symmetry, heteroatoms, fused rings, and the interaction between C1−C4 atoms affect the band gap of an aromatic form in the opposite way as they do the gap of a quinonoid form. In general, it has been recognized that the more stable an isomer is, the larger its band gap.[28−33] That is, if we try to decrease through structural modifications the band gap of an isomer that is stable in the ground state, the other isomer becomes more stable and its band gap becomes larger. This leads to a difficulty in designing a small band-gap polymer with a nondegenerate π-conjugated system. Actually, our previous analysis has indicated that the band gaps (defined as $\lambda_{\max}$ values) of heterocyclic polymers in the ground state can rarely be achieved below 1 eV, due to the transition between the aromatic and quinonoid forms.[34]

Contrary to heterocyclic conjugated polymers, *trans*-polyacetylene (*t*-PA) is doubly degenerate in the ground state. That is, two isomeric structures have the same electronic characters. Therefore, if we modify the structure of *t*-PA for exploring a small band-gap polymer, we can avoid the problem that was found in heterocyclic conjugated systems. As shown in Figure 1, polypentafulvalene (PFV) is degenerate in the ground state and thus must be a good starting material for structural modifications in the designing of a very small band-gap polymer. In this study, we investigated the electronic properties of structurally modified PFVs, as well as PFV itself, to search for small band-gap polymers. Pentafulvalene, first prepared by Doering and Matzner,[35] is known to be extremely unstable, but its substituted derivatives with halogens,[36] phenyl,[37] or *tert*-butyl group[38] and its ring-fused derivatives[39] form solid crystals that are stable toward light and air. However, to our knowledge, no oligomers or polymers of pentafulvalene systems have experimentally been prepared. Lowe et al. theoretically investigated the electronic structure of poly(cyclopentadienyl), namely, an undimerized PFV, and predicted that the polymer would possess a zero band gap.[40] In the first part of this paper, we present the electronic structures of PFV and substituted PFVs with electron-donating (methoxy) and -accepting (cyano) groups. Both groups are known to decrease the band gap of poly(phenylenevinylene).[41] Methoxy groups lead to an asymmetric destabilization of the LUMO and HOMO levels of the polymer backbone, the latter being more elevated.[42] On the other hand, cyano substitution induces an asymmetric and stronger stabilization of the frontier MO levels, the LUMO level being more depressed.[43] Alkoxy substitution has experimentally been observed to decrease band gaps of a variety of conjugated polymers.[44] In the second part, we describe the effect of a variety of fused rings on the electronic structure of PFV.

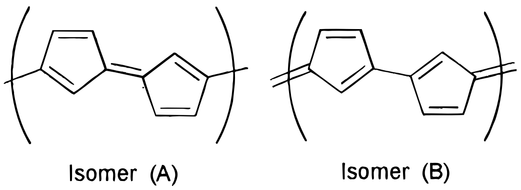
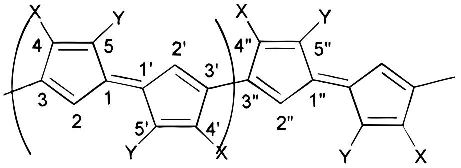


Figure 1. Two degenerate structures of polypentafulvalene.

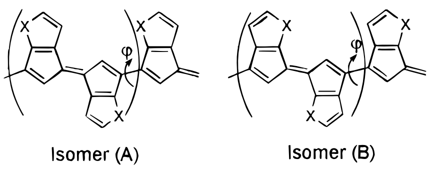
---

[18] Kertesz, M.; Lee, Y.-S. *J. Phys. Chem.* **1987**, *91*, 2690.
[19] Toussaint, J. M.; Brédas, J. L. *Macromolecules* **1993**, *25*, 5240.
[20] Hong, S. Y.; Song, J. M. *Synth. Met.* **1996**, *83*, 141.
[21] Jira, R.; Bräunling, H. *Synth. Met.* **1987**, *17*, 691.
[22] Chen, W.-C.; Jenekhe, S. A. *Macromolecules* **1995**, *28*, 465.
[23] Kürti, J.; Surján, P. R.; Kertesz, M. *J. Am. Chem. Soc.* **1991**, *113*, 9865.
[24] Kürti, J.; Surján, P. R.; Kertesz, M.; Frapper, G. *Synth. Met.* **1993**, *55−57*, 4338.
[25] Hong, S. Y.; Kwon, S. J.; Kim, S. C. *J. Chem. Phys.* **1996**, *104*, 1140.
[26] Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.
[27] Hong, S. Y.; Song, J. M. *Chem. Mater.* **1997**, *9*, 297.
[28] Hong, S. Y.; Marynick, D. S. *Macromolecules* **1995**, *28*, 4991.
[29] Hong, S. Y.; Kwon, S. J.; Kim, S. C. *J. Chem. Phys.* **1995**, *103*, 1871.
[30] Lee, Y.-S.; Kertesz, M.; Elsenbaumer, R. L. *Chem. Mater.* **1990**, *2*, 526.
[31] Hong, S. Y.; Marynick, D. S. *Macromolecules* **1992**, *25*, 4652.
[32] Hong, S. Y.; Song, J. M. *J. Phys. Chem. B* **1997**, *101*, 10249.
[33] Hong, S. Y.; Song, J. M. *J. Chem. Phys.* **1997**, *107*, 10607.
[34] Hong, S. Y.; Kwon, S. J.; Kim, S. C.; Marynick, D. S. *Synth. Met.* **1995**, *69*, 701.
[35] Doering, W. von E. *Theoretical Organic Chemistry*; Butterworth: London, 1959; p 35. Matzner, E. Ph.D. Thesis, Yale University, 1958.
[36] Fallon, L.; Ammon, H. L.; West, R.; Rao, V. N. M. *Acta Crystallogr. B* **1974**, *30*, 2407. Kwistowski, P. T.; West, R. *J. Am. Chem. Soc.* **1966**, *88*, 4541. Ginsberg, A. E.; Paatz, R.; Korte, F. *Tetrahedron Lett.* **1962**, 779. Mark, V. *Tetrahedron Lett.* **1961**, 333.
[37] Prinzbach, H.; Sauter, H. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 133.
[38] Brand, R.; Krimmer, H.-P.; Lindner, H.-J.; Sturm, V.; Hafner, K. *Tetrahedron Lett.* **1982**, *23*, 5131.
[39] Escher, von A.; Neuenschwander, M.; Engel, P. *Helv. Chim. Acta* **1987**, *70*, 1623. Bergmann, E. D. *Chem. Rev.* **1968**, *68*, 41.
[40] Lowe, J. P.; Kafafi, S. A.; LaFemina, J. P. *J. Phys. Chem.* **1986**, *90*, 6602.
[41] Cornil, J.; dos Santos, D. A.; Beljonne, D.; Brédas, J. L. *J. Phys. Chem.* **1995**, *99*, 5604.
[42] Meyers, F.; Heeger, A. J.; Brédas, J. L. *J. Chem. Phys.* **1992**, *97*, 2750.
[43] Fahlman, M.; Brédas, J. L. *Synth. Met.* **1996**, *78*, 39.
[44] Lee, G. J.; Yu, S. K.; Kim, D. H.; Lee, J.-L.; Shim, H.-K. *Synth. Met.* **1995**, *69*, 431. Liang, W. B.; Lenz, R. W.; Karasz, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2867. Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281. Woo, H. S.; Graham, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Phys. Rev. B* **1992**, *46*, 7379. Eckhardt, H.; Shaklette, L. W.; Jen, K. Y.; Elsenbaumer, R. L. *J. Chem. Phys.* **1989**, *91*, 1303.



X, Y = H : polypentafulvalene (PFV)
X = OMe, Y = H : poly(4,4'-dimethoxypentafulvalene) (4MxPFV)
X = H, Y = OMe : poly(5,5'-dimethoxypentafulvalene) (5MxPFV)
X = CN, Y = H : poly(4,4'-dicyanopentafulvalene) (4CNPFV)
X = H, Y = CN : poly(5,5'-dicyanopentafulvalene) (5CNPFV)

Figure 2. Polypentafulvalenes investigated in this study.



Isomer (A) Isomer (B)

Figure 3. Polypentafulvalene systems fused with vinylene−X fragments (X = O, S, NH).

Methodology

To obtain ground-state structures of the polymers, depicted in Figures 2 and 3, we performed band calculations at the Austin model 1 (AM1) level, which is implemented by MOSOL,[45] the solid-state version of semiempirical methods. This version adopts the Born−von Kármán periodic boundary condition and Bloch functions for crystal calculations. The AM1 method is known to produce quite satisfactory conformational behaviors for a variety of conjugated molecules in comparison with ab initio and experimental data, although the method yields low rotational barriers.[46] However, quantum-mechanical calculations for one polymer chain may not correctly produce the conformations for the condensed phase because the calculations do not include interchain interactions. Packing of polymer chains would increase planarity of a polymer in the condensed phase. Therefore, examining a potential energy surface with respect to torsion angles is more informative in order to understand the conformations of polymers in the condensed phase than just locating the global minimum.

First, we optimized the geometric parameters (bond length and bond angles) for the planar conformations. Six representative wave vectors (k) were chosen from 0 to π/a (a is the unit cell length) with regular intervals. The neighboring unit cells as far as the third-nearest ones were involved in the lattice sum. A calculation for PFV with a large set of wave vectors (21k points) and neighboring unit cells (6 unit cells on each side of the central unit) essentially produced the same results: the differences in energy, bond lengths, and bond angles were less than 0.01 kcal/mol of unit cells, 0.001 Å, and 0.05°, respectively. Then, to examine the conformational behavior, we took a unit cell twice as large as the one for the planar form and constructed a potential energy curve with respect to the torsion angle (φ) between the fulvalene units. Total energies of the twisted structures were calculated just by varying the torsion angle by 10°, from 0° to 90°, with the other geometric parameters not optimized. If an energy minimum is found, the geometric parameters for the twisted structure were fully optimized to compare the energy with that for the planar conformation.

It is well-known that Hartree−Fock (HF) level calculations greatly overestimate the band gaps (E_gs) of conjugated polymers: the gaps being taken as the HOMO−LUMO gaps.[47] It is expected that the calculated band gaps would be comparable with the experimental values if electron correlation effects are properly considered. Recently, Brédas and co-workers have calculated vertical excitation energies of conjugated oligomers by incorporating excited states through an intermediate neglect of the differential overlap/configuration interaction technique.[48] The extrapolated transition energies for the corresponding polymers have been estimated in quite good agreements with the experimental observations, although the lowest S_0-S_1 transitions have been ascribed to exciton transitions, not to interband transitions. On the other hand, lower-level approaches such as VEH,[49] Hückel, and EH methods[50] have produced reasonable band gaps of one-dimensional conjugated polymers in comparison with the experimental values owing to parametrizations, although these approaches do not explicitly include electron correlation effects. In this study, electronic properties of the polymers were obtained by applying the AM1 optimized structures to the MEH method.[17] The MEH method adopts the off-diagonal elements into a new form, which has an additional distance-dependent empirical factor. This approach was parametrized to reproduce band gaps defined as the λ_{max} for the $\pi-\pi^*$ transition of conjugated polymers, and not the band edges, as are often used to define the gaps experimentally. Typically, the band edge is about 0.5 eV lower than the peak value. There has been some experimental evidence to support our choice of a band gap as the λ_{max} value. A photoconduction study of *t*-PA and polydiacetylene (PDA) has revealed that the band gaps of the polymers are larger than the absorption edge value because the onsets of the photoconductivity action spectra have been found at energies higher than that of the edges.[51] Electron-energy-loss spectroscopic (EELS) investigations of *t*-PA, PDA, polyparaphenylene (PPP), and polyphenylenevinylene (PPV) have demonstrated that the lowest absorption peak of the UV−vis spectrum is momentum-dependent but the edge is not.[52] Therefore, it has been concluded that the former arises from the interband transition and the latter is due to the localized excitonic state. Recently, momentum dependence of the peaks of PPP and PPV has been reproduced through quantum-mechanical calculations.[48b,53] Comparison between the reflectance and electro-reflectance spectra of PDA has also led to the same conclusion as the EELS investigations.[54] Photoluminescence (PL) spectra of polythiophene have also confirmed that the absorption edge is related to the excitonic state because the PL peak due to the localized excitonic state has been found near the edge.[55] Smearing-out of an absorption band may arise from interactions between one-dimensional chains of a polymer and from interactions associated with phonons. Exciton binding energies of conjugated polymers have experimentally been estimated to be near 0.5 eV,[56] although in some cases they were reported to be either less than 0.2

---

(45) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902. Stewart, J. J. P. *QCPE Bull.* **1985**, *5*, 62. Cui, C. X.; Kertesz, M. *J. Am. Chem. Soc.* **1989**, *111*, 4216.

(46) Fabian, W. M. F. *J. Comput. Chem.* **1988**, *9*, 369.

(47) Suhai, S. *Phys. Rev. B* **1983**, *27*, 3506. Kertesz, M. *Adv. Quantum Chem.* **1982**, *15*, 61. Ford, W. K.; Duck, C. B.; Salaneck, W. R. *J. Chem. Phys.* **1982**, *77*, 5030.

(48) Brédas, J. L.; Cornil, J.; Beljonne, D.; dos Santos, D. A.; Shuai, Z. *Acc. Chem. Res.* **1999**, *32*, 267. Beljonne, D.; Cornil, J.; Friend, R. H.; Janssen, R. A. J.; Brédas, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6453. Beljonne, D.; Shuai, Z.; Friend, R. H.; Brédas, J. L. *J. Chem. Phys.* **1995**, *102*, 2042. (b) Brocorens, P.; Zojer, E.; Cornil, J.; Leising, G.; Müllen, K.; Brédas, J. L. *Synth. Met.* **1999**, *100*, 141.

(49) Brédas, J. L.; Chance, R. R.; Silbey, R.; Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1981**, *75*, 225. Nicolas, G.; Durand, Ph. *J. Chem. Phys.* **1979**, *70*, 2020.

(50) Whangbo, M. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 6093. Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(51) Donovan, K. J.; Wilson, E. G. *J. Phys. C* **1979**, *12*, 4857. Yee, K. C.; Chance, R. R. *J. Polym. Sci., Polym. Phys.* **1978**, *16*, 431. Chance, R. R.; Baughman, R. H. *J. Chem. Phys.* **1976**, *64*, 3899.

(52) Fink, J. *Synth. Met.* **1987**, *21*, 87. Ritsco, J. J.; Crecelius, G.; Fink, J. *Phys. Rev. B* **1983**, *27*, 4902. Ritsco, J. J.; Mele, E. J.; Heeger, A. J.; MacDiarmid, A. G.; Ozaki, M. *Phys. Rev. Lett.* **1980**, *44*, 1351.

(53) Shuai, Z.; Zojer, E.; Leising, G.; Brédas, J. L. *Synth. Met.* **1999**, *101*, 337.

(54) Sebastian, L.; Weiser, G. *Chem. Phys.* **1981**, *62*, 447; *Phys. Rev. Lett.* **1981**, *46*, 1156.

(55) Kaneto, K.; Yoshino, K. *Synth. Met.* **1989**, *28*, C287. Sauvajol, J. L.; Chenouni, D.; Hasoon, S.; Lere-Porte, J. P. *Synth. Met.* **1989**, *28*, C293. Shinar, J.; Vardeny, Z.; Ehrenfreund, E.; Brafman, O. *Synth. Met.* **1987**, *18*, 199. Vardeny, Z.; Ehrenfreund, E.; Shinar, J.; Wudl, F. *Phys. Rev. B* **1987**, *35*, 2498.

Table 1. Valence Shell Atomic Parameters Used in the Modified Extended Hückel Band Calculations: Ionization Potentials (IP in eV), and Slater Orbital Exponents (ζ in au)

atom	n	l	IP	ζ	n	l	IP	ζ
H	1	0	13.60	1.300				
C	2	0	21.40	1.625	2	1	11.40	1.625
N	2	0	26.00	1.950	2	1	13.40	1.950
O	2	0	32.30	1.975	2	1	14.80	1.975
O[a]	2	0	32.30	2.275	2	1	14.80	2.275
S	3	0	20.0	2.117	3	1	13.30	2.117

[a] Parameters for oxygen in the methoxy group.

Table 2. Optimized Geometric Parameters for the Planar Conformation of PFVs in Figure 2[a]

	PFV	4M×PFV	5M×PFV	4CNPFV	5CNPFV
R(1−2)	1.477	1.478	1.476	1.474	1.480
R(2−3)	1.373	1.373	1.374	1.374	1.372
R(3−4)	1.485	1.492	1.478	1.495	1.477
R(4−5)	1.361	1.371	1.368	1.371	1.372
R(1−1′)	1.342	1.344	1.341	1.343	1.346
R(3′−3″)	1.426	1.426	1.427	1.432	1.426
θ(2−3−4)	108.3	107.0	108.7	107.3	108.2
θ(3−4−5)	108.9	109.7	108.1	109.1	108.9
θ(1−5−4)	108.6	108.0	109.6	108.5	108.8
θ(1′−1−5)	127.2	127.4	128.1	127.1	128.9
θ(3″−3′−4′)	123.6	124.9	123.4	125.4	123.7
δr[b]	0.098	0.097	0.097	0.096	0.099

[a] Bond lengths are in angstroms, and bond angles are in degrees. [b] Average value of the bond-length alternation; defined as $\delta r = |R(2-3) - R(1-2) + R(1-1') - R(1'-2') + R(2'-3') - R(3'-3'')|/3$.

Table 3. Electronic Properties (in eV) of *t*-PA[a] and PFVs in the Planar Conformation

	t-PA	PFV	4MxPFV	5MxPFV	4CNPFV	5CNPFV
E_g [b]	1.55	1.13	1.39	0.75	0.99 [c]	1.12
E_{HOMO}	−11.32	−12.07	−11.87	−11.53	−12.09	−12.13
E_{LUMO}	−9.77	−10.94	−10.48	−10.78	−11.10	−11.01
HVBW[d]	5.47	0.70	0.24	0.62	0.66	0.60
LCBW [e]	2.36	1.70	1.91	2.13	1.31	1.29

[a] Data from Hong.[62] [b] Band gap; defined as the $\lambda_{\max}$ for the $\pi-\pi^*$ transition. [c] At the optimized torsion angle of 31.7°, E_g = 1.20 eV. [d] HVBW = highest valence bandwidth. [e] LCBW = lowest conduction bandwidth.

eV[57] or as large as 0.8 eV.[58] The MEH method has predicted the values of band gaps within an error of ca. 10% (less than 0.3 eV) compared to the experimental values[17,33,59] and produced band structures of poly(*p*-phenylene) and poly(*p*-phenylenevinylene) in excellent agreements with EELS measurements.[60] MEH parameters used in the calculations are listed in Table 1.

Polypentafulvalenes

In the planar conformation of PFV, the distance between two hydrogen atoms bonded at C4′ and C2″ atoms is calculated to be 2.40 Å, which is the same as double the van der Waals (vdW) radius (1.2 Å)[61] for hydrogen. Therefore, it is expected that the vdW repulsion between the hydrogen atoms is negligible and that the planar conformation is quite stable due to the π-conjugation between the fulvalene units. In fact, the AM1 optimization revealed that PFV would be of the planar conformation in the ground state. Optimized geometric parameters and calculated electronic properties for the planar conformation of PFV are given with those of substituted PFVs in Tables 2 and 3, respectively. PFV is predicted to exhibit a band gap of 1.13 eV, smaller than the gap of *t*-PA, by 0.4 eV, although the former is calculated to possess a bond-length alternation (δr) of 0.098 Å, similar to the value (0.096 Å)[62] for the latter. As shown in Figure 4, this results from the strong bonding interactions between the frontier orbitals of the *t*-PA-like backbone and the high-lying π^* orbitals of the vinylene fragments. These interactions lower the HOMO and the LUMO levels as much as 0.77 and 1.17 eV, respectively. Therefore, it is expected that PFV is less susceptible to oxidation but more susceptible to reduction than *t*-PA. Because the π^* orbital of the fragment is closer in energy to the LUMO of the backbone than it is to the HOMO, the interaction is stronger with the LUMO than with the HOMO, and thereby, the LUMO is more stabilized. However, the bandwidths of PFV, particularly the highest valence bandwidth (HVBW), become very narrow compared to that of *t*-PA. Figure 5 shows the MEH-calculated π-band structure of PFV. When a symmetry is imposed so as to remove Peierls distortion [that is, $R(1-2) = R(2-3) = R(1'-2') = R(2'-3')$ and $R(1-1') = R(3'-3'')$], the band gap completely disappears as Lowe et al. predicted for poly(cyclopentadienyl).[40] This implies

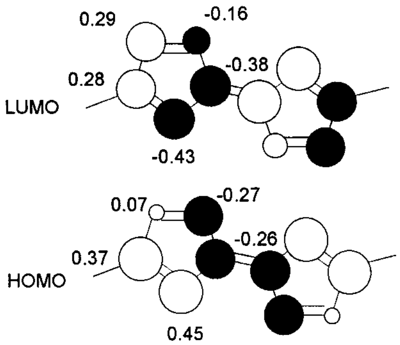


Figure 4. Highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO) for PFV.

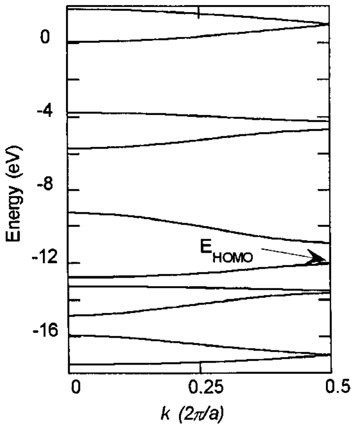


Figure 5. MEH-calculated π-band structure of PFV.

---

(56) Alvarado, S. F.; Seidler, P. F.; Lidzey, D. G.; Bradley, D. D. C. *Phys. Rev. Lett.* **1998**, *81*, 1082. Tasch, S.; Ekström, O.; Jost, T.; Scherf, U.; Leising, G. *Synth. Met.* **1997**, *85*, 1251. Mizes, H. A.; Conwell, E. M. *Synth. Met.* **1995**, *68*, 145.

(57) Yang, Y.; Pei, Q.; Heeger, A. J. *Synth. Met.* **1996**, *78*, 263.

(58) Shinar, J. *Synth. Met.* **1996**, *78*, 277.

(59) Hong, S. Y. *Bull. Korean Chem. Soc.* **1999**, *20*, 42.

(60) Czerwinski, W.; Nücker, N.; Fink, J. *Synth. Met.* **1988**, *25*, 71. Fink, J. *Synth. Met.* **1987**, *21*, 87.

(61) *Handbook of Chemistry and Physics*, 70th ed.; CRC Press, Inc.: Boca Raton, Florida, 1990.

(62) Hong, S. Y. *Bull. Korean Chem. Soc.* **1995**, *16*, 845.

from the geometrical viewpoint that the band gap of PFV originates entirely from the bond-length alternation (δr) along the *t*-PA-like conjugated backbone.

Because disubstitution breaks the symmetry of PFV, a 4,4′-disubstituted PFV is the nondegenerate isomer of a 5,5′-disubstituted PFV. However, it is predicted that electronic structures of the isomers do not significantly differ. Table 2 shows that substituting with methoxy or cyano groups does not basically alter the geometric structures of the conjugated PFV backbone, although it does slightly elongate the C4−C5 and C4′−C5′ bonds. In contrast, as shown in Table 3, electronic properties of the substituted PFVs are somewhat different from the property of PFV itself and depend on the substitutional site. Frontier orbitals of PFV in Figure 4 demonstrate that in the HOMO the contributions from the π-type p orbitals of C5 and C5′ atoms are much larger than those of C4 and C4′ atoms, whereas in the LUMO, it is just the opposite. Therefore, stronger interactions are expected to occur between the HOMO of PFV and the π-type orbitals of substituents bonded at C5 and C5′ and between the LUMO and the π-type orbitals of substituents bonded at C4 and C4′. Because the low-lying π-type p orbitals of oxygen atoms in the methoxy substituents interact in an antibonding way with the frontier orbitals of the PFV backbone, poly(5,5′-dimethoxypentafulvalene) (5MxPFV) possesses a high HOMO level and a small band gap in comparison with unsubstituted PFV. On the other hand, poly(4,4′-dimethoxypentafulvalene) (4MxPFV) exhibits a high LUMO level and a large band gap. The lower HOMO level of 4MxPFV could explain why 4MxPFV is more stable, by about 2.2 kcal/mol of fulvalene units, than 5MxPFV. It is noteworthy that the band gap (0.75 eV) of 5MxPFV is only half the value of *t*-PA. When cyano groups are substituted, the situation becomes reversed, because the high-lying π^* orbitals of the groups interact in a bonding way with the frontier orbitals of the PFV backbone. Accordingly, compared to PFV, poly(4,4′-dicyanopentafulvalene) (4CNPFV) exhibits a slightly lower LUMO level and a smaller band gap. In poly(5,5′-dicyanopentafulvalene) (5CNPFV), it is found that the HOMO is stabilized as much as is the LUMO, and thus, the band gap has a value similar to that of PFV. It is estimated that 5CNPFV is slightly more stable than 4CNPFV, by ca. 1.2 kcal/mol of fulvalene units.

AM1 optimizations predicted that the dimethoxy-substituted PFVs would be planar in the ground state. In 4MxPFV, the shortest distance between oxygen in the methoxy group and hydrogen in the neighboring unit is computed to be 2.30 Å, which is much smaller than the sum (2.6 Å) of the vdW radii for oxygen and hydrogen atoms.[61] Therefore, it is expected that π-conjugation between the fulvalene units is so strong as to keep two units on the same plane. The strong tendency toward planarity has also been observed in methoxy-substituted poly(*p*-phenylenevinylenes).[59] In Figure 6 a potential energy minimum for 4CNPFV appears at a torsion angle of about 30°, due to the strong steric repulsion between the cyano group and hydrogen in the neighboring unit. AM1 full optimizations demonstrated that the twisted conformation of 4CNPFV, with an optimized torsion angle of 31.7°, would be nearly isoenergetic with the planar conformation of 5CNPFV. The AM1 study of a three-ring oligomer for cyano-substituted PPV has also shown a large torsion angle of ca. 30° between the phenylene ring and the vinylene group.[43] No appreciable change in the geometric structures was observed between planar and twisted conformations. The band gap for the twisted conformation of 4CNPFV is calculated to be 1.20 eV.

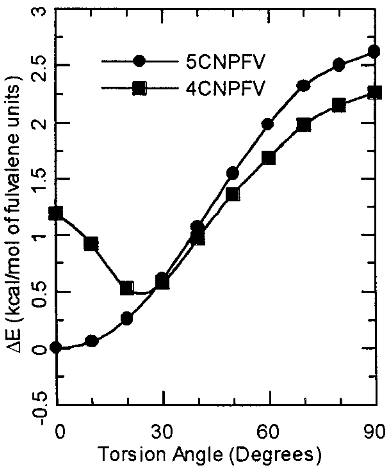


Figure 6. Torsion potential curves for 4CNPFV and 5CNPFV.

Table 4. Electronic Properties (in eV) for the Planar Conformation of Ring-Fused PFVs in Figure 3

	PFPFV		PTPFV		PPPFV	
	(A)	(B)	(A)	(B)	(A)	(B)
E_g	1.17	1.15	1.09	1.08[a]	1.12[b]	1.10
E_{HOMO}	−11.57	−11.60	−11.59	−11.60	−11.44	−11.45
E_{LUMO}	−10.40	−10.45	−10.49	−10.52	−10.32	−10.35
HVBW	0.28	0.28	0.45	0.45	0.36	0.36
LCBW	2.24	2.22	1.99	1.95	2.26	2.23

[a] At the optimized torsion angle of 22.2°, E_g = 1.19 eV. [b] At the optimized torsion angle of 25.7°, E_g = 1.29 eV.

Polypentafulvalene Systems Fused with Vinylene−X Fragments

As depicted in Figure 3, degeneracy of PFV is removed in the PFV systems fused with vinylene−X (X = O, S, or NH) groups. AM1 optimizations for the planar conformation revealed, regardless of X, that isomer A would be slightly more stable than isomer B. However, the energy difference (ΔE) between these isomers is estimated to be small or negligible: ΔE = 1.12, 0.05, and 0.64 kcal/mol of fulvalene units for X = O, S, and NH, respectively. There are also no appreciable differences in geometric and electronic structures between these isomers. The δr values of the polymers are calculated to be nearly the same as the value of PFV. As presented in Table 4, in comparison with unsubstituted PFV, the ring-fused PFV systems exhibit similar band gaps, in the range of 1.08−1.17 eV, but high HOMO and LUMO levels. These predictions can be understood by looking at the π orbitals of the vinyleneoxy fragment, in Figure 7. Geometrical parameters for the fragment were extracted from the polymer structure in order to obtain the π orbitals of the fragment. Because in the frontier orbitals of PFV backbone MO coefficients of C4 are opposite in sign to those of C5, only the π_2 orbital of the fragment strongly interacts with the frontier orbitals of the PFV backbone. The interactions

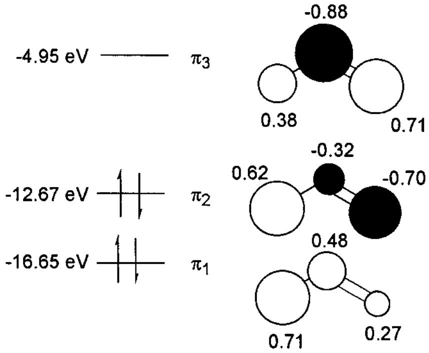


Figure 7. π-Energy levels (in eV) and orbitals of the vinylene-oxy fragment.

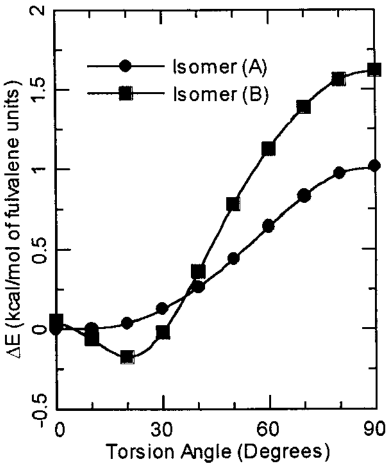


Figure 8. Torsion potential curves for PTPFV isomers.

occur in an antibonding way, because the π_2 orbital lies in energy below the frontier orbitals. Both the HOMO and the LUMO of poly(difuranopentafulvalene) [PFPFV] are destabilized, by as much as 0.5 eV. Similar interactions are also found in poly(dithienopentafulvalene) [PTPFV] and poly(dipyrrolopentafulvalene) [PPPFV].

Conformations of the fused PFV systems would be determined by the shortest distance between X and H in the neighboring units in isomer A and between two H atoms in the neighboring units in isomer B. If the distance is much shorter than the sum of the vdW radii for the elements, the polymer chains would be twisted to reduce the vdW repulsion between the atoms. Otherwise, the polymers would be planar due to the π-conjugation between the fulvalene units. The vdW radii for H, O, and S are 1.2, 1.40, and 1.85 Å, respectively.[61] In the planar conformation of isomer A, the shortest X···H distances are calculated to be 2.72 Å in PFPFV, 2.76 Å in PTPFV, and 2.18 Å in PPPFV. The AM1 calculations show that, in isomeric structure A, PFPFV is planar and PPPFV is twisted, as expected. However, structure A of PTPFV is predicted to be planar despite the very short S···H distance. As shown in Figure 8, the potential energy difference between the planar and the 50°-twisted conformations is less than 0.5 kcal/mol of unit cells. The potential curve for the isomer A of PPPFV in Figure 9 shows that the 25°-twisted conformation is only about 0.3 kcal/mol of fulvalene unit more stable than the planar one. In the planar structure of isomer B, the shortest H···H distances are predicted to be 2.33 Å in PFPFV, 2.04 Å in PTPFV, and 2.28 Å in PPPFV. Only PTPFV is twisted at a torsion angle of about 20°. In the condensed phase, the isomer A of PPPFV and the isomer B of PTPFV are also expected to be nearly planar due to the small energy barriers over the planar conformation.

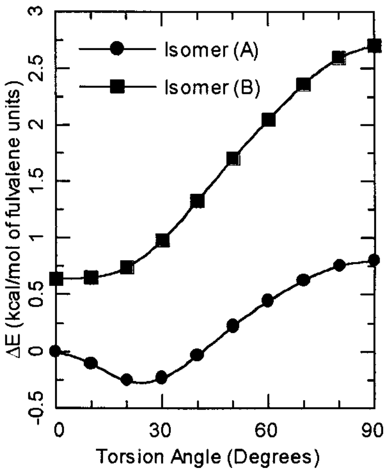


Figure 9. Torsion potential curves for PPPFV isomers.

Conclusions

By incorporating vinylene fragments onto a *t*-PA backbone, we introduced novel stable and small band-gap PFV systems. In these systems, both HOMO and LUMO levels of the *t*-PA-like backbone are stabilized through bonding interaction with the π^* orbital of the vinylene fragment. Therefore, in comparison with *t*-PA, these polymers are predicted to exhibit relatively large stability against oxidative environments, as well as small band gaps.

PFV was estimated to possess a band gap of 1.13 eV. A further decrease in the band gap can be achieved by substituting either methoxy groups at C5 and C5′ or cyano groups at C4 and C4′. The different behavior with respect to the substituents comes from the fact that, in the HOMO of PFV, π-contributions from C5 and C5′ atoms are larger than those from C4 and C4′ atoms, whereas in the LUMO, it is just the opposite. Therefore, the methoxy groups bonded at C5 and C5′ sites more strongly destabilize the HOMO than the LUMO, and the cyano groups bonded at C4 and C4′ sites more strongly stabilize the LUMO than the HOMO. Because the vinylene−X fragments interact simultaneously with both carbon atoms, both the HOMO and the LUMO of the PFV backbone are destabilized by the same amount. Therefore, fusion of the vinylene−X fragments hardly affects the band gap of PFV.

Acknowledgment. The authors acknowledge the financial support of the Korea Research Foundation made in the program (1997-001-D00265) of 1997.

CM990496N