

# The Frequency-Dependent First-, Second-, and Third-Order Polarizabilities of Thiophene-, Furan-, Pyrrole-Nitro Polyene Systems

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The semiempirical time-dependent Hartree-Fock PM3 calculations have been performed on three polyene systems. In order to study the nonlinear optical properties, we calculated the frequency-dependent first-, second-, and third-order polarizabilities of thiophene-, furan-, pyrrole-nitro polyene systems. The PM3 predicted average and longitudinal polarizabilities increase in the order: thiophene->pyrrole->furan-nitro polyene systems. The PM3 predicted limiting average second-order polarizabilities show the order: pyrrole->furan->thiophene-nitro polyene systems. The average and longitudinal third-order polarizabilities have the following order: pyrrole->thiophene->furan-nitro polyene systems. In these trends, we suggest that pyrrole group is the best donor group among the three polyene systems.

## Introduction

Materials comprising electron donor-acceptor molecules have attracted much attentions due to their large second-order nonlinear optical properties.<sup>1,2</sup> Recently, organic compounds containing heterocyclic moieties (thiophene, pyrrole, furan) are well known to exhibit significant NLO behavior and may play an important role in photonic technology.<sup>3-5</sup>

The large second-order polarizabilities originate from strong charge-transfer interaction in the donor and acceptor molecules which enhance the electronic polarization induced by incident laser light. Therefore, it is of important to design the adequate donor-acceptor (DA) molecules. Bella *et al.*<sup>6</sup> reported that the second-order nonlinear optical response of model molecular 1:1 and asymmetric 2:1 organic  $\pi$  electron donor-acceptor (EDA) complexes is investigated using the INDO/S sum-over-excited particle-hole-states formalism. Also, they reported that the role and nature of intermolecular interactions in determining quadratic nonlinear optical macroscopic hyperpolarizabilities were investigated on clusters (dimers and trimers) of archetypical donor/acceptor organic  $\pi$  electron chromophore molecules. Meyers *et al.*<sup>7</sup> have reported ab initio-CPHF calculations on the series of benzodithia and dithiolene polyenals. The authors concluded that the sulfur ring groups behave as electron donors in all molecules in that study.

The polydiacetylene systems have attracted particular attention and are expected as the materials having large third-order nonlinear characteristics. Kirtman and Hasan<sup>8</sup> calculated the static longitudinal third-order polarizabilities,  $\gamma$ , for the polydiacetylene and polybutatriene oligomers through  $C_{26}H_{16}$  by the coupled-perturbed-Hartree-Fock(CPHF)<sup>9-12</sup> method in both the INDO<sup>13</sup> and ab initio formalisms.

There are a number of semiempirical calculations of hyperpolarizabilities. For example, the NLO properties for benzene and stilbene derivatives<sup>14</sup> and push-pull polyenes have been performed using the Pariser-Parr-Pople(PPP) method. CNDO calculations of NLO properties have been performed on urea,<sup>15</sup> benzene derivatives,<sup>16,17</sup> and polyphenyls and polyenes.<sup>18</sup> INDO calculations of NLO properties have also been performed for substituted benzenes<sup>19</sup> and polyenes.<sup>20</sup> MNDO calculations of these properties were performed for substitu-

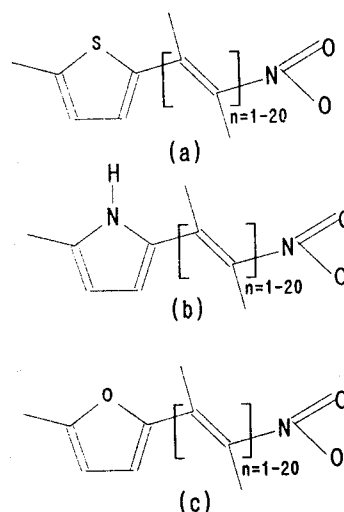


Figure 1. Structures of thiophene-(a), pyrrole-(b), furan-(c) nitro polyene systems.

ted polyenes<sup>21</sup> by using the AM1 parametrization.

## Methods

In this paper, the time-dependent Hartree-Fock semiempirical PM3 calculations were employed to obtain the first-, second-, and third-order frequency dependent polarizabilities for the thiophene-(a), furan-(b), and pyrrole-(c) nitro polyenes of the varying chain length  $N$  shown in Figure 1. The quantum chemistry program MOPAC'93 was used.

The energy  $E(E)$  of a molecular system perturbed by an external electric field  $E$  can be written as:

$$E(E) = E^0 - \mu_a E^a - (2!)^{-1} \alpha_{ab} E^a E^b - (3!)^{-1} \beta_{abc} E^a E^b E^c - (4!)^{-1} \gamma_{abcd} E^a E^b E^c E^d$$

where the summation over the repeated indices is implied. The indices  $a, b, c, d, \dots = x, y, z$ . In the above equation,  $\mu_a$  is the a component of the dipole moment,  $\alpha_{ab}$ ,  $\beta_{abc}$ , and  $\gamma_{abcd}$  are first-, second-, third-order polarizability tensors, respectively. The second-order polarizability for the static case is denoted

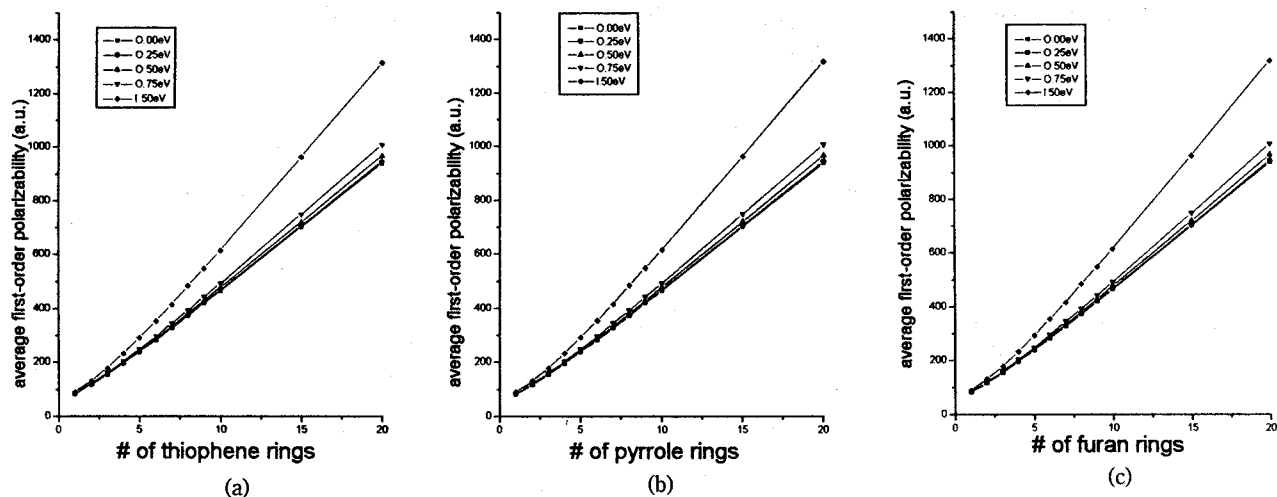


Figure 2. The PM3-calculated average first-order polarizabilities for thiophene (a), pyrrole (b), and furan (c)-nitro polyenes.

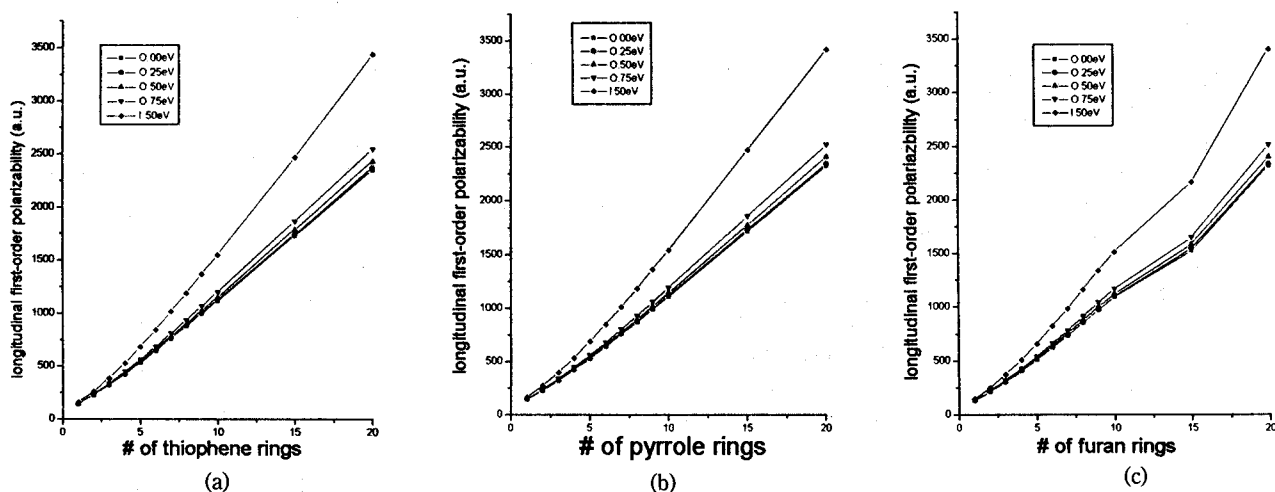


Figure 3. The PM3-calculated longitudinal polarizabilities for thiophene (a), pyrrole (b), and furan (c)-nitro polyenes.

as  $\beta(0; 0,0)$  and that for second-harmonic generation (SHG), it is denoted as  $\beta(-2\omega; \omega,\omega)$ . The static and third-harmonic generation (THG) are denoted  $\gamma(0; 0,0,0)$  and  $\gamma(3\omega; \omega,\omega,\omega)$ , respectively. The average polarizability is  $\langle\alpha\rangle = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ . The vector component of the second-order polarizability tensor is  $\beta_i = 2/5(\beta_{i11} + \beta_{i22} + \beta_{i33})$ . The average second-order polarizability,  $\langle\gamma\rangle$ , is given by  $\langle\gamma\rangle = 1/5(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$ .

Considering donors (thiophene, furan, pyrrole rings) and acceptor (nitro group) in which molecular components to possess  $C_{2v}$  symmetry, the resulting thiophene-, furan-, pyrrole-nitro polyene systems possess  $C_s$  symmetry. The thiophene-, furan-, and pyrrole-nitro polyenes were fully optimized. All vibrational frequencies had positive values.

The limiting values for the thiophene-, furan-, pyrrole-nitro polyenes have been estimated by extrapolation. In this study, the extrapolation procedure is applied by the following formula

$$\log A(N) = a + b/N + c/N^2 + d/N^3$$

where  $N$  is the number of the unit  $C=C$  bonds and  $A(N)$

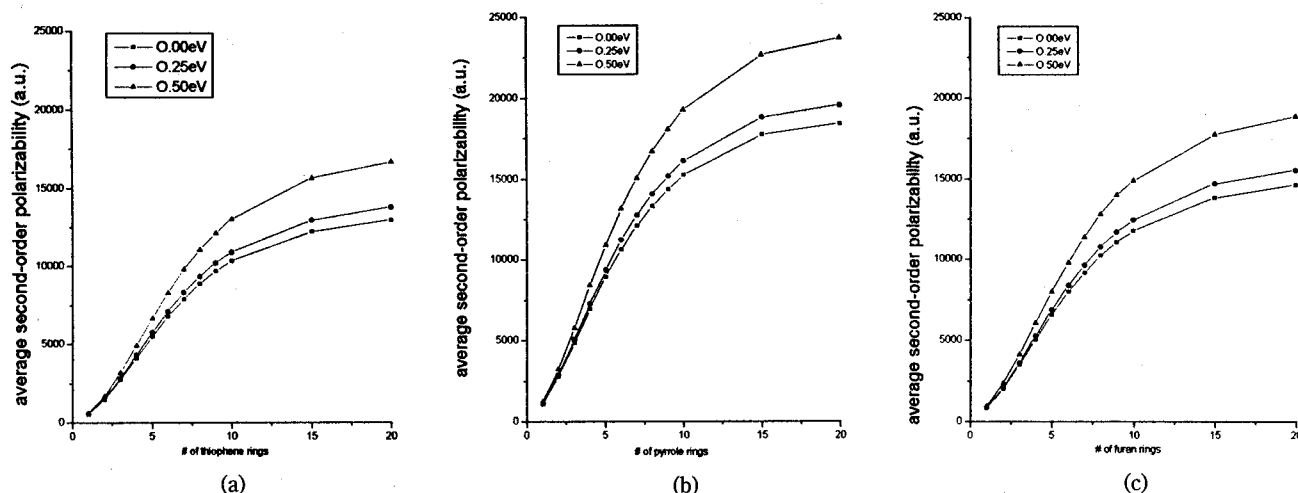
is the  $\langle\alpha\rangle$ ,  $\alpha_{xx}$ ,  $\beta$ , and  $\langle\gamma\rangle$ ,  $\gamma_{xxxx}$ . The extrapolated values for infinite thiophene-, furan-, and pyrrole-nitro polyenes are  $A(\infty) = 10^3$ .

It is reported that the extrapolated  $\langle\alpha\rangle$ ,  $\alpha_{xx}$ ,  $\beta$ ,  $\langle\gamma\rangle$ , and  $\gamma_{xxxx}$  values have considerably large uncertainties. Therefore, the  $\langle\alpha\rangle$ ,  $\alpha_{xx}$ ,  $\beta$ , and  $\langle\gamma\rangle$ ,  $\gamma_{xxxx}$  values would have to be evaluated by the semiempirical PM3 calculation for the long chain lengths in order to obtain reliable  $\langle\alpha\rangle$ ,  $\alpha_{xx}$ ,  $\beta$ ,  $\langle\gamma\rangle$ , and  $\gamma_{xxxx}$  values.

## Results and Discussion

PM3-predicted first-order average and longitudinal polarizabilities of thiophene-, furan-, pyrrole-nitro polyene systems for the frequencies of the 0.0 eV, 0.25 eV, 0.5 eV, 0.75 eV, and 1.5 eV are represented in Figures 2 and 3, respectively.

The PM3 asymptotic average (longitudinal) limiting values of thiophene-nitro polyene systems for the frequencies of 0.0 eV, 0.25 eV, 0.5 eV, 0.75 eV, and 1.5 eV are 1110.06 (2784.26), 1118.48 (2808.50), 1160.29 (2883.90), 1191.87 (3019.98), and 1563.45 (4084.20), respectively.



**Figure 4.** The PM3-calculated average second-order polarizabilities for thiophene (a), pyrrole (b), and furan (c)-nitro polyenes.

In the furan-nitro polyene systems, PM3 asymptotic average(longitudinal) limiting values for the frequencies of 0.0 eV, 0.25 eV, 0.5 eV, 0.75 eV, and 1.5 eV are 1095.15 (2659.32), 1103.49 (2685.77), 1129.41 (2758.58), 1176.15 (2887.28), and 1544.01 (3899.20), respectively. These values are slightly smaller than those of thiophene-nitro systems.

On the other hand, PM3 asymptotic average (longitudinal) limiting values of pyrrole-nitro polyene systems for the frequencies of 0.0 eV, 0.25 eV, 0.5 eV, 0.75 eV, and 1.5 eV are 1100.14 (2765.65), 1108.49 (2789.65), 1134.50 (2864.68), 1181.38 (2999.82), and 1550.41 (4067.83), respectively. Comparing with thiophene-nitro polyene systems, these values are slightly smaller. However, these values are slightly larger than those of furan-nitro polyene systems.

These Results show that PM3-predicted average and longitudinal linear polarizabilities increase in the order: thiophene->pyrrole->furan-nitro polyene systems. In this paper, PM3 calculated average linear polarizabilities for the thiophene-, furan-, pyrrole-nitro polyene systems at the static frequency are larger than nonsubstituted-, methyl-fluoro-, and amino-nitro-polyenes.<sup>22</sup>

PM3-predicted second-order polarizabilities of thiophene-, furan-, pyrrole-nitro polyene systems for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are represented in Figure 4.

In the thiophene-nitro polyene systems, the limiting second-order polarizabilities (exponents values) for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are 1.68e4 (1.10), 1.79e4 (1.11), and 2.18e4 (1.15), respectively. The exponent values are about two times smaller than previous experimental studies on  $\pi$ -electron polyenic systems in which the estimated exponent values are 2.1,<sup>23</sup> 2.4,<sup>24</sup> and 3.4.<sup>25</sup> We predicted that the second-order polarizabilities,  $\beta$ , reached an optimum value in the thiophene-nitro polyene systems near  $N=20$ , as represented in Figure 3(a). These results were in agreement with the CNDOVSB-derived results on the conjugation length for dimethylamino-nitro polyene systems. On the other hand, These saturated conjugation lengths are slightly longer than dimethylamino-nitro polyphenyl systems.<sup>26</sup>

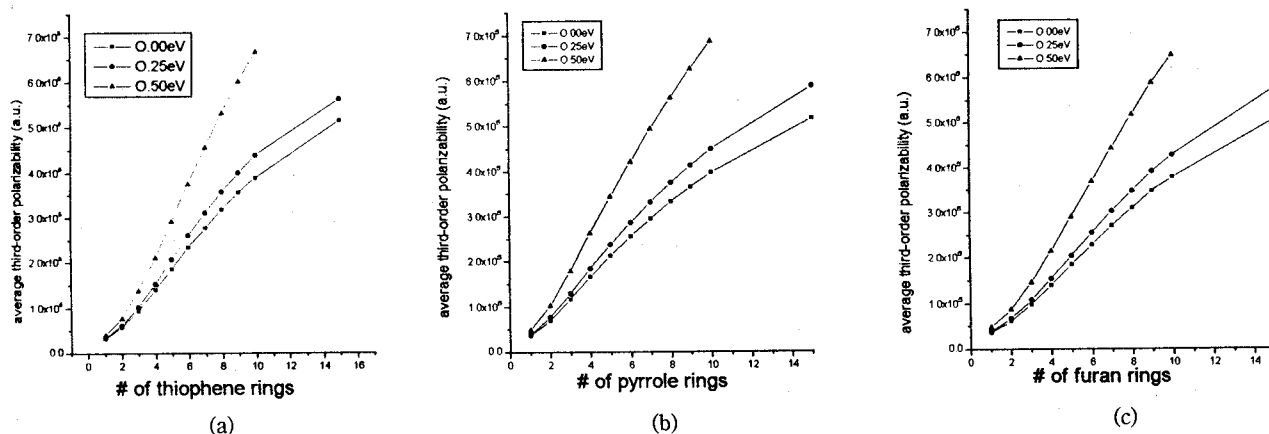
Karna *et al.*<sup>27</sup> reported that the molecular second-order nonlinear optical coefficient,  $\beta$ , as determined by the EFISHG, for 2-nitro-1-(2-thienyl)ethene and 4-nitro-1-(2-thienyl)-

1,3-butadiene are, respectively, 1 and 3 times that of p-nitroaniline. Also, the Mulliken population analysis indicated that the sulfur atom in the thiophene ring acts as the electron donor, whereby a migration of charge takes place from the thiophene ring to the electron withdrawing nitro group. Comparing with the EFISHG (Electric Field Induced Second Harmonic Generation) measurements values for  $N=1$  and  $N=2$ , PM3-calculated second-order polarizabilities,  $\beta$  are, respectively, about 1.5 times smaller. Also, PM3-calculated values are underestimated compared with the ab initio STO-3G, 4-31G, 4-31G+ $d_{sd}$ , 4-31G+ $d_{diff}$  values.

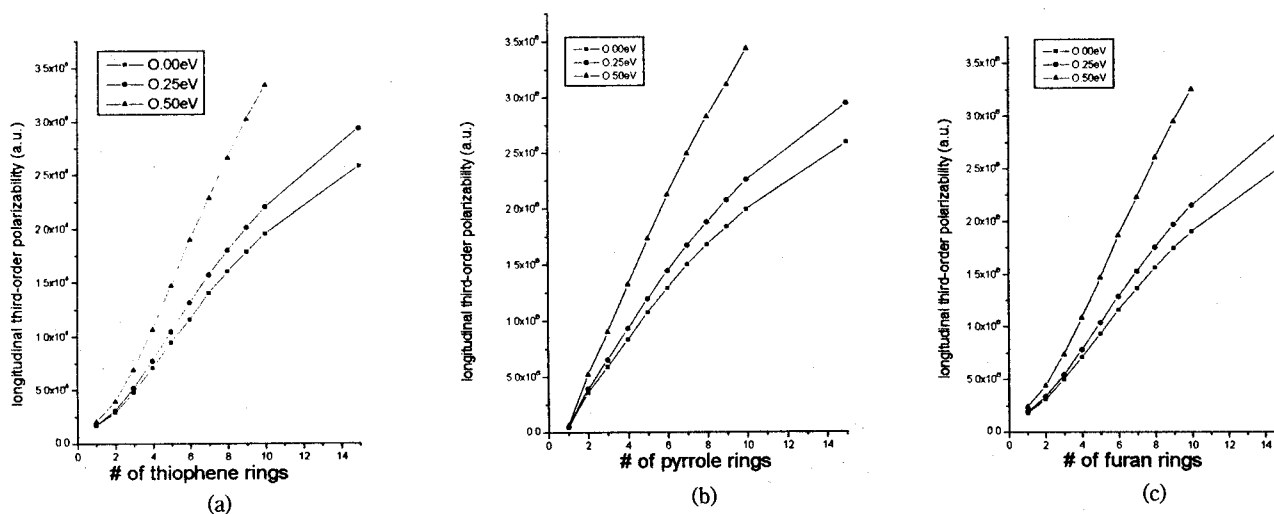
In the pyrrole-nitro polyene systems, the limiting second-order polarizabilities (exponents values) for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are 2.34e4 (0.98), 2.49e4 (0.99), and 3.03e4 (1.02), respectively. The limiting values of pyrrole-nitro polyene systems for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are slightly larger compared with the limiting values of thiophene-nitro polyene systems. On the other hand, the exponent values are slightly smaller than those of thiophene-nitro polyene systems.

In the furan-nitro polyene systems, the limiting second-order polarizabilities (exponents values) for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are 1.88e4 (1.00), 2.00e4 (1.01), and 2.44e4 (1.04), respectively. These values are slightly larger than the second-order polarizabilities of thiophene-nitro polyenes. On the other hand, these values are smaller than those of pyrrole-nitro polyenes. Also, compared with p-nitro aniline, the second-order polarizabilities are 1.5 times smaller.

The saturated second-order polarizabilities ( $N=20$ ) for the pyrrole-nitro, furan-nitro, and thiophene-nitro polyenes were 2.37e4, 1.88e4, and 1.67e4 at 0.5 eV, as shown in Figure 4, respectively. Also, The PM3-predicted limiting average second-order polarizabilities showed the following order: thiophene-<furan-<pyrrole-nitro polyene systems. Therefore, we predicted that pyrrole group was the most strong donor in thiophene, furan, pyrrole heterocyclic rings. From Figure 4, we have observed a strong length dependence of  $\beta$  up to  $N=9$  (the number of C=C bonds) but a weak one for  $N>9$ . We have demonstrated that the pyrrole group is superior to a furan and thiophene group for achieving a large second-



**Figure 5.** The PM3-calculated average third-order polarizabilities per unit cell of thiophene (a), pyrrole (b), and furan (c)-nitro polyenes.



**Figure 6.** The PM3-calculated longitudinal third-order polarizabilities per unit cell of thiophene (a)-, pyrrole (b)-, and furan (c)-nitro polyenes.

order polarizability.

The delocalized  $\pi$ -electrons affect extremely large longitudinal hyperpolarizabilities. Recently, a number of ab initio and semi-empirical theoretical studies have been carried out.<sup>28-30</sup> Melo *et al.* have performed theoretical calculations of the third-order polarizabilities for regular polyene, soliton-like polyene, and polaron like polyene at Pariser-Parr-Pople (PPP) level.<sup>13</sup>

PM3-predicted third-order average and longitudinal polarizabilities of thiophene-, furan-, pyrrole-nitro polyene systems for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are represented in Figures 5 and 6, respectively.

In the pyrrole-nitro polyene systems, the third-order average asymptotic polarizabilities for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are  $1.05e7$  (2.02),  $1.20e7$  (2.04), and  $1.28e7$  (2.17), respectively. Also, third-order longitudinal asymptotic polarizabilities for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are  $5.28e7$  (2.37),  $6.00e7$  (2.39), and  $6.40e7$  (2.57), respectively. In the thiophene-nitro polyene systems, the third-order PM3 asymptotic average (longitudinal) polarizabilities for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are  $1.06e7$

( $5.30e7$ ),  $1.20e7$  ( $6.02e7$ ), and  $1.26e7$  ( $6.34e7$ ), respectively. The static average third-order polarizabilities for  $N=1$  ( $32\ 000$  a.u.) and  $N=2$  ( $113600$  a.u.) (the number of C=C bonds) are underestimated in comparison with DFWM (degenerate four wave mixing) experimental value ( $N=1$ ;  $47514$  a.u.,  $N=2$ ;  $134800$  a.u.). The average and longitudinal third-order polarizabilities for thiophene-nitro polyenes are somewhat smaller than those for the pyrrole-nitro polyenes.

In the furan-nitro polyene systems, the third-order PM3 asymptotic average (longitudinal) polarizabilities for the frequencies of 0.0 eV, 0.25 eV, and 0.5 eV are  $1.03e7$  ( $5.18e7$ ),  $1.17e7$  ( $5.89e7$ ), and  $1.23e7$  ( $6.14e7$ ), respectively. The third-order asymptotic average and longitudinal polarizabilities of the furan-nitro polyenes are the smallest values among the three polyenes. The average third-order polarizabilities of thiophene-, furan-, and pyrrole-nitro polyenes are two orders of magnitude larger than amino-nitro polyenes, methyl-fluoro polyenes, and unsubstituted polyenes.<sup>22</sup>

The extrapolated longitudinal third-order polarizabilities for thiophene-, furan-, pyrrole-nitro polyenes are one order of magnitude larger than the unsubstituted polyenes, unsubstituted

tuted polydiacetylenes, donor-acceptor polydiacetylenes<sup>8</sup> when Hurst *et al.* extrapolation procedure<sup>9</sup> was applied.

In conclusion, PM3 predicted average first-order polarizabilities increase in the order: thiophene->pyrrole->furan-nitro polyenes. On the other hand, longitudinal polarizabilities show the order: pyrrole->thiophene->furan-nitro polyenes. The predicted limiting average second-order polarizabilities have the following order: pyrrole->furan->thiophene-nitro polyenes. The third-order average and longitudinal polarizabilities have the order: pyrrole->thiophene->furan-nitro polyenes. From the above results, we suggest that pyrrole group is the best donor group among the three polyene systems.

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