

## Infrared Absorption Spectroscopic Studies of $\alpha,\omega$ -Diphenylpolyenyl Anions with Odd Numbered Polyene Molecules

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Infrared absorption spectra of  $\alpha,\omega$ -diphenylpolyenyl anions  $\text{Ph}(\text{CH})_n\text{Ph}^-$  ( $\text{DP}_n^-$ ,  $n=7, 9,$  and  $13$ ) in the tetrahydrofuran- $d_6$  solutions was measured in the range of  $1700$  and  $1200\text{ cm}^{-1}$ . The infrared spectra obtained from anions ( $\text{DP}_n^-$ ) showed considerable difference from their neutral species ( $\text{DP}_n$ ): their intensities were enhanced at least two orders of magnitude stronger than their neutral species. The in-plane CH bending modes at  $1464$  and  $1375\text{ cm}^{-1}$  are correspondingly strengthened with the chain length increased, but the C=C stretching at  $1541\text{ cm}^{-1}$  is weakened and frequencies are not changed. We provide an IR evidence for the first time that the bond order or bond alternations of the anions (soliton) are different from those of radical anions (polaron) as well as neutral species.

**Keywords :** Soliton,  $\alpha,\omega$ -Diphenylpolyenyl amines, Infrared spectroscopy.

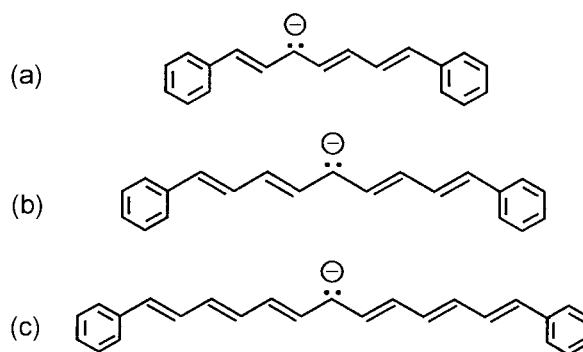
### Introduction

The structures and properties of conjugated polymers have been studied by various spectroscopic techniques. Infrared (IR) spectroscopy is increasingly being used as a powerful tool for studying conducting polymers, because it gives us knowledge on molecular structures of transient states as well as their dynamic properties. Various studies have been performed with the vibrational modes around a soliton in *trans*-polyacetylene (*trans*-PA), since three infrared absorption peaks of lightly doped-PA were observed at  $1397, 1288,$  and  $888\text{ cm}^{-1}$ .<sup>1</sup> Su *et al.*<sup>2</sup> reported that the charged solitons which have charges but no spin act as the spinless charged carriers when the dopant content is below the critical value, 6 mol %. Zannoni and Zerbi<sup>3</sup> have calculated the densities of the vibrational states of doped-PA using the force constant method, and Peluso *et al.*<sup>4</sup> have obtained the force constants using the cluster model by the MNDO method. Previous studies<sup>5</sup> showed that static charges and charge fluxes were the main factors to interpret the spectroscopic data of frequencies and intensities, and the calculations of inter-atomic distances and bond energies; they are also useful for the determination of intra-molecular<sup>6</sup> and inter-molecular<sup>7,8</sup> interactions. Mori *et al.*<sup>9</sup> suggested based on the MNDO method that the trends in wavenumbers are similar for positively and negatively charged solitons, and one of the wavenumbers is particularly sensitive to conjugation length. MO calculations by *ab initio* method (6-31G) also indicate the dispersion of wavenumbers with conjugation lengths.<sup>10</sup> Nonetheless, infrared spectra of any charged species have not been reported in experimental method yet. More recent studies have been focused on the charge-storage mechanism in short polyenes and diphenylpolyenes,<sup>11-13</sup> which can be considered as oligomers of poly-

acetylene. Interest in the structural and spectral characteristics of the charged species (anions, radical anions and divalent ions) of conjugated compounds has been increasing from both the experimental and theoretical points of view. Studies on the charged species of oligo- and polyene compounds in particular are not only interesting in themselves but also important for understanding the electrical properties of doped PA.

In this paper, IR spectra with a model compounds of a negative soliton in *trans*-PA,  $\alpha,\omega$ -diphenylpolyenyl anions,  $\text{Ph}(\text{CH})_n\text{Ph}^-$  ( $\text{DP}_n^-$ ,  $n=7, 9,$  and  $13$ ; see Figure 1), are reported. The molecular structures of  $\text{DP}_n^-$  are schematically shown in Figure 1.

These compounds with odd numbers of carbons at the polyene parts have a negative charge, but no spin. Tolbert *et al.*<sup>11</sup> have been also reported the NMR and electronic absorption spectra of  $\alpha,\omega$ -diphenylpolyenyl anions,  $\text{Ph}(\text{CH})_n\text{Ph}^-$  (abbreviated as  $\text{DP}_n^-$ ,  $n=3, 5, 7, 9, 13,$  and  $17$ ), as the good model compounds for the negative soliton in *trans*-PA. For the comparison, IR spectra of the radical anions,  $\text{DP}_n^{\bullet-}$  ( $n$  is 6, 8, and 10), as the model compounds for the negatively



**Figure 1.** Molecular structures of  $\alpha,\omega$ -diphenylpolyenyl anions ( $\text{DP}_n^-$ ): (a)  $\text{DP}_7^-$ , (b)  $\text{DP}_9^-$ , and (c)  $\text{DP}_{13}^-$ .

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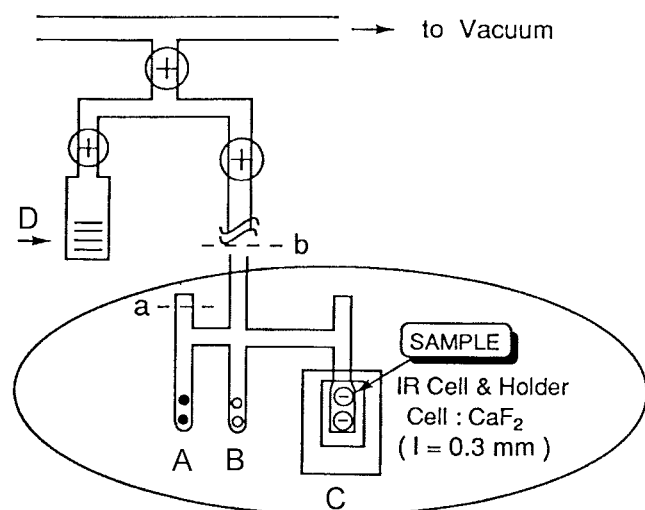
charged polarons in *trans*-PA are also measured between 1700 and 1200  $\text{cm}^{-1}$ .

### Experimental Section

The  $\alpha,\omega$ -diphenylpolyenyl anions ( $\text{DP}_n^-$ ,  $n=7, 9$ , and 13) and their neutral species ( $\text{DP}_n$ ) were prepared using the previously reported methods.<sup>11,14,15</sup> A *n*-butyllithium (Aldrich) was supplied as a 1.6 molar solution in *n*-hexane. This reducing agent is well known to produce the  $\text{DP}_n^-$  anion solutions (THF- $d_6$ ) which are free of ion pairing.<sup>15</sup> Solutions of  $\text{DP}_n^-$  were prepared under high vacuum in Pyrex apparatus with specially designed  $\text{CaF}_2$  infrared (IR) cell as shown in Figure 2.

A weighed quantity of polyene ( $\text{DP}_n$ ), 1.6 mol *n*-Butyllithium/*n*-hexane, and THF- $d_6$  solvents were put into the tube A, B, and D, respectively. C is the  $\text{CaF}_2$  infrared cell (path length is 0.3 mm) with modified vacuum tight holder. This apparatus for the sampling of anions ( $\text{DP}_n^-$ ) was completely sealed and connected with the high vacuum line. The *n*-hexane solution of *n*-butyllithium was removed under vacuum and replaced with the THF- $d_6$  solvents from tube D by the distillation method. The synthesis of  $\text{DP}_n^-$  were carried out by contacting *n*-butyllithium (B in Figure 2) with  $\text{DP}_n$  (A in Figure 2) and THF- $d_6$  solvents.

After the reaction (reduction), the sampling apparatus detached from the vacuum line (the position b in Figure 2) and the  $\text{DP}_n^-$  solutions were introduced into the IR cell of part C. The concentration of sample in the THF- $d_6$  solution was  $10^{-5}$ - $10^{-4}$  mol/ $\text{dm}^3$  range. The reduction reactions were identified from the change of electronic absorption spectra. All-*trans*- $\text{DP}_n$  ( $n=6, 8$ , and 10: even number) were purchased from the Tokyo Chemical Industry, Ltd. and Aldrich Chemical Co., respectively, and used without further purification. The radical anions ( $\text{DP}_n^{\bullet-}$ ;  $n=6, 8$ , and 10) in each polyene were prepared by reducing the neutral polyene in



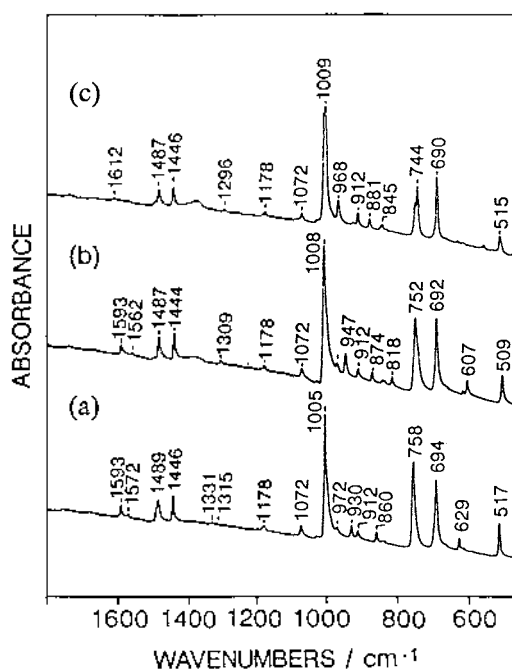
**Figure 2.** Apparatus for obtaining anion samples for infrared spectra; A:  $\text{DP}_n$  sample tube, B: *n*-Butyllithium tube or sodium mirror, C:  $\text{CaF}_2$  infrared cell (path length is 0.3 mm) and holder, D: solvent tube.

THF- $d_6$  solution in a tube B of sodium mirror.

Infrared absorption spectra were measured by a JEOL JIR 5500 FT-IR spectrophotometer with a MCT detector. The difference spectrum between  $\text{DP}_n^-$  in THF- $d_6$  solutions and pure THF- $d_6$  solvents are measured into the  $\text{CaF}_2$  infrared cell between 1700  $\text{cm}^{-1}$  and 1200  $\text{cm}^{-1}$  regions. Hitachi U-3500 spectrophotometer was used for the electronic absorption spectra.

### Results and Discussion

The reduction process can be identified by electronic absorption spectroscopy. The electronic absorption of  $\text{DP}_n^-$  shows a strong single absorption band attributed to the  $n-\pi^*$  electronic transition between the nonbonding orbital and the  $\pi^*$  LUMO orbital. According to the MO energy level diagram, the non-bonding orbital which is occupied by two non-bonding electrons exists in the middle of the band gap. The maximum absorption band is shifted to a lower energy region with the increase of polyene chain length. These electronic absorption band characteristics of  $\text{DP}_n$  in the THF- $d_6$  solution are similar with that in the DMSO solution.<sup>11</sup> Our electronic absorption data are also consistent with the theoretical results using a continuum model, in which the soliton in PA is expected to have only one electronic absorption band at the mid-gap center. On the other hand, the radical anions of  $\alpha,\omega$ -diphenylpolyene and  $\alpha,\omega$ -dibutylpolyene are known to have two absorption bands caused by the  $\pi-\pi^*$  transition ( $1^3B_g \rightarrow 2^2A_u$  and  $1^3B_g \rightarrow 1^2A_u$ ). In case of *trans*-PA, electronic transition to the soliton and transitions due to vibrations around a soliton are observed in the infrared spectrum.<sup>1,16,17</sup> These are at 1397, 1288, and 888  $\text{cm}^{-1}$  for



**Figure 3.** Infrared spectra (1700-500  $\text{cm}^{-1}$ ) of  $\alpha,\omega$ -diphenylpolyene ( $\text{DP}_n$ ,  $n$  is even numbered carbon): (a)  $\text{DP}_6$ , (b)  $\text{DP}_8$ , and (c)  $\text{DP}_{10}$ , measured in KBr disk.

**Table 1.** Observed infrared frequencies of  $\alpha,\omega$ -diphenylpolyenes and its assignments ("reference 18)

Mode	$\alpha,\omega$ -Diphenylpolyene (DPn)			Ref. 18		Assignment
	DP6	DP8	DP10	Obs.	Cal.	
<i>bu</i> $\nu_1$	1593	1593	1612	1626	1627	$\nu$ (C=C)
$\nu_2$	1572	1562	—	1595	1586	$\nu$ (C=C)
$\nu_3$	1489	1487	1487	—	—	Phenyl group
$\nu_4$	1446	1444	1446	1417	1422	$\delta$ (CH)
$\nu_5$	1331	—	—	1320	1309	$\delta$ (CH)
$\nu_6$	1315	1309	1296	1279	1282	$\delta$ (CH)
$\nu_7$	1178	1178	1178	1153	1141	$\nu$ (C-C)
$\nu_8$	1072	1072	1072	—	—	Phenyl group
<i>au</i> $\nu_9$	1005	1008	1009	1010	1020	$\tau$ (C=C)
$\nu_{10}$	972	972	968	972	978	$\gamma$ (CH)
<i>bu</i> $\nu_{11}$	930	947	—	945	947	$\nu$ (C-C)
<i>au</i> $\nu_{12}$	912	912	912	918	922	$\gamma$ (CH)
$\nu_{13}$	860	874	881	899	894	$\gamma$ (CH)
$\nu_{14}$	—	818	845	863	852	$\gamma$ (CH)
$\nu_{15}$	758	752	744	—	—	Phenyl group
$\nu_{16}$	694	692	690	—	—	Phenyl group
$\nu_{17}$	629	607	—	651	642	$\gamma$ (CH)
$\nu_{18}$	517	509	515	—	—	$\gamma$ (CH)

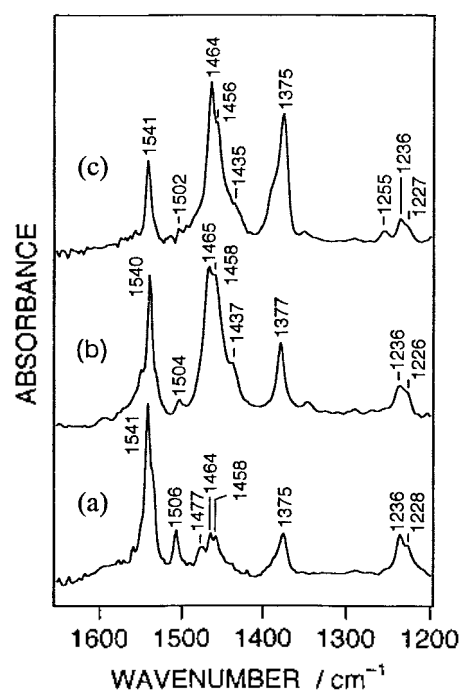
Ref. 18: Observed and calculated vibrational frequencies of all-*trans*-1,3,5,7,9-decapentaene.

(CH)<sub>n</sub> and at 1140 and 790 cm<sup>-1</sup> for (CD)<sub>n</sub> with lightly iodine doped *trans*-PA.<sup>1</sup>

The FT-IR spectra of DP<sub>n</sub> (n is 6, 8, and 10) in KBr disk between 500 and 1700 cm<sup>-1</sup> are shown in Figure 3(a), (b), and (c), respectively. The tentative assignments of the bands observed from all-*trans*-DP<sub>n</sub> are listed in Table 1. In Table 1, the vibrational bands of DP<sub>n</sub> (n is 6, 8, and 10) are in good agreement with the results of all-*trans*-1, 3, 5, 7, 9-decapentaene calculated at the MP2/6-31G level and its observed data.<sup>18</sup> From this result, each infrared peak of DP<sub>n</sub> can be assigned. In the infrared spectrum of DP<sub>n</sub> (n is 7, 9, and 13; Figure 3), the most intensive band is observed at the 1005-1009 cm<sup>-1</sup> range ( $\nu_9$ ). This band is assigned to the out-of plane CH deformation or C=C wagging. Another C=C stretches bands are also observed between 1562 and 1612 cm<sup>-1</sup> ( $\nu_1$  and  $\nu_2$ ), although its intensities are very weak. The weak infrared band at 1178 cm<sup>-1</sup> mainly consists of the C-C stretches and the in-plane CH bends ( $\nu_7$ ). The 930(DP<sub>6</sub>) and 947(DP<sub>8</sub>) cm<sup>-1</sup> ( $\nu_{11}$ ) are the C-C stretches bands. The bands between 1446 and 1296 cm<sup>-1</sup> ( $\nu_4$ ,  $\nu_5$  and  $\nu_6$ ) can be assigned to the in-plane CH bending, and bands between 912 and 515 cm<sup>-1</sup> ( $\nu_{12}$ ,  $\nu_{13}$ ,  $\nu_{14}$ ,  $\nu_{17}$  and  $\nu_{18}$ ) to the out-of plane CH bending, respectively. In particular, the  $\nu_3$ ,  $\nu_8$ ,  $\nu_{15}$  and  $\nu_{16}$  bands are induced from phenyl groups.

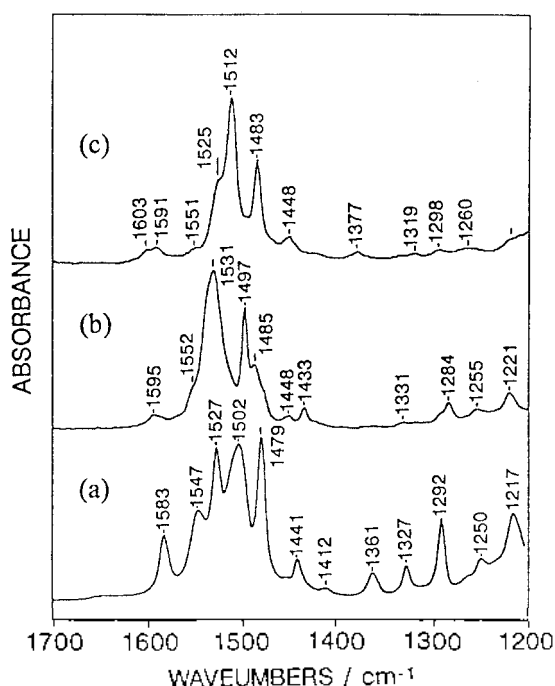
The FT-IR spectra of DP<sub>n</sub><sup>-</sup> (n is 7, 9, and 13) measured between 1700 and 1200 cm<sup>-1</sup> are shown in Figure 4(a), (b), and (c), respectively.

As show in Figure 3 and 4, the infrared spectra of anions (Figure 4) are quite different with its neutral species (Figure 3). Although detailed spectrum analysis of the observed anions is not possible at the present stage, the following



**Figure 4.** Infrared spectra (1700-1200 cm<sup>-1</sup>) of  $\alpha,\omega$ -diphenylpolyenyl anions (DP<sub>n</sub><sup>-</sup>) in THF-d<sub>6</sub> solutions; (a) DP<sub>7</sub><sup>-</sup> ( $0.8 \times 10^{-4}$ ), (b) DP<sub>9</sub><sup>-</sup> ( $0.1 \times 10^{-4}$ ), and (c) DP<sub>13</sub><sup>-</sup> ( $0.02 \times 10^{-4}$  mol/cm<sup>3</sup>), measured in CaF<sub>2</sub> infrared cell, respectively. Solvent bands are subtracted.

points could be mentioned. In Figure 4, the peaks between 1502 and 1541 cm<sup>-1</sup> are assigned to the C=C stretching mode, and the relative intensity decrease regularly with chain length (n) increases, but the wavenumbers are not changed. These peak positions are about 45-50 cm<sup>-1</sup> lower than the corresponding band of its neutral states ( $\nu_1$  and  $\nu_2$  bands in Figure 3). According to the MNDO calculations on the anions of C<sub>5</sub>H<sub>7</sub> to C<sub>33</sub>H<sub>35</sub> reported by Mori *et al.*,<sup>9</sup> infrared wavenumbers in this region were not particularly sensitive to the conjugation length, and its relative intensities. In doped polyacetylene,<sup>1</sup> the C=C stretching band was not found in this region. The peaks between 1375 and 1465 cm<sup>-1</sup> are assigned as the CH bending mode, and their relative intensities are increased drastically with the chain length increase, but the wavenumbers are not changed. According to the calculation results by Mori *et al.*,<sup>9</sup> the CH bending modes for the cations of C<sub>13</sub>H<sub>15</sub>, C<sub>17</sub>H<sub>19</sub> and C<sub>33</sub>H<sub>35</sub> have been reported at 1397, 1376 and 1358 cm<sup>-1</sup>, respectively. These bands are corresponding to the 1397 cm<sup>-1</sup> band in the lightly iodine doped *trans*-PA.<sup>1</sup> The frequency of this band depends upon the effect of electron-phonon interaction. Piaggio *et al.*<sup>19</sup> reported that the infrared peak of 1397 cm<sup>-1</sup> in doped PA shifts appreciably toward higher frequencies as the length of the conjugated sequences is shortened. The corresponding band in photo-induced PA have been also reported at 1369 cm<sup>-1</sup>.<sup>20</sup> We indicate that the relative intensities of CH bending peaks are very sensitive with the change of chain lengths, but their wavenumbers are not. Especially, a peak at 1375 cm<sup>-1</sup> is stronger than 1465 cm<sup>-1</sup> as the polyene chain length (n) increases from 7 to 13. For the comparison, FT-IR



**Figure 5.** Infrared spectra (1700-1200  $\text{cm}^{-1}$ ) of radical anions of  $\alpha,\omega$ -diphenylpolyene ( $\text{DP}_n^{\bullet-}$ ) in  $\text{THF-d}_6$  solutions; (a)  $\text{DP}_6^{\bullet-}$  ( $0.5 \times 10^{-4}$ ), (b)  $\text{DP}_8^{\bullet-}$  ( $0.4 \times 10^{-4}$ ), and (c)  $\text{DP}_{10}^{\bullet-}$  ( $0.2 \times 10^{-4}$  mol/ $\text{cm}^3$ ), measured in  $\text{CaF}_2$  infrared cell, respectively. Solvent bands are subtracted.

spectra of the radical anions of  $\text{DP}_n$  ( $\text{DP}_n^{\bullet-}$ ;  $n$  is 6, 8, and 10) as the model compounds of a negatively polaron in *trans*-PA measured between 1700 and 1200  $\text{cm}^{-1}$  are also shown in Figure 5(a), (b), and (c), respectively.

The IR spectra of the polaron models ( $\text{DP}_n^{\bullet-}$ ) are quite different with those of the soliton models ( $\text{DP}_n^-$ ). But, the CH bending modes of  $\text{DP}_n^{\bullet-}$  observed between 1433 and 1552  $\text{cm}^{-1}$  are 50-80  $\text{cm}^{-1}$  higher frequency regions than corresponding bands of  $\text{DP}_n^-$ . We could not find the corresponding band at around 1397  $\text{cm}^{-1}$  on the doped *trans*-PA. The C=C stretching peak (1593-1531  $\text{cm}^{-1}$ ) are weaker than those of the soliton models ( $\text{DP}_n^-$ ). The variance of spectrum between  $\text{DP}_n^-$  and  $\text{DP}_n^{\bullet-}$  indicates that the bond orders or bond alternations of the anions (soliton models) are somewhat different from those of radical anions (polaron models) as well as its neutral species.

In Figure 4, the bands of 1226 and 1236  $\text{cm}^{-1}$  may be associated with CH in-plane bending of benzene rings (end groups) with charge. The corresponding peaks of the 1288  $\text{cm}^{-1}$  (C-C stretching) and 888  $\text{cm}^{-1}$  (C=C stretching) in doped PA could not be clearly observed because a limit of the  $\text{CaF}_2$  IR cell and solvent system used in this experiment. The infrared spectra obtained from anions ( $\text{DP}_n$ ) or radical anions ( $\text{DP}_n^{\bullet-}$ ) have been shown a considerable difference with its neutral species ( $\text{DP}_n$ ), and their IR intensities are enhanced at least two orders of magnitude stronger than its

neutral species.

Anyway, as described above, the charge-induced IR bands of  $\text{DP}_n$  are clearly different from those of charge and spin-induced  $\text{DP}_n$ . Tentative assignments for the observed bands have been discussed on the base of results obtained in the all-*trans*-1, 3, 5, 7, 9-decapentaene calculated at the MP2/6-31G level<sup>18</sup> and the MNDO calculations on the anions of  $\text{C}_3\text{H}_7$  to  $\text{C}_{33}\text{H}_{35}$ .<sup>9</sup> However, for the more correct discussion about the differentia of structural and vibrational characteristics between anions (soliton) and radical anions (polaron) of  $\text{DP}_n$ , the MO calculations of  $\text{DP}_n$  and  $\text{DP}_n^{\bullet-}$  at the high level are need, and more extensive studies for longer chain compounds are absolutely needed to clearly understand the self-localized charge domains in doped PA because Su<sup>2</sup> and Kivelson<sup>9</sup> have been actually proposed the soliton and polaron lattice structures in doped PA, respectively.

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