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Theoretical Study on Static Second Hyperpolarizabilities for Several π-Conjugated Systems Including Nitrogen Atoms: Effects of Charged Defects and Extension of π-Conjugation

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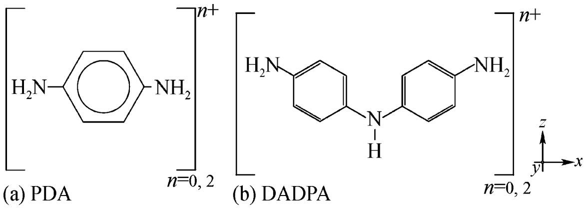
We investigated static second hyperpolarizabilities (γ) of 1,4-phenylendiamine (PDA) and 4,4′-diaminodiphenylamine (DADPA) by using the ab initio molecular orbital (MO) methods. The DADPA molecule is assumed to have a planar structure, in which two PDA are linked by a central nitrogen (N) atom, and is considered to be the simplest model for extended dendrimers including linking N atoms. We also examined dicationic PDA and DADPA in order to clarify the effects of charged defects in π-conjugated systems on γ values. The γ value is shown to be enhanced nonlinearly by linking two π-conjugated units via an N atom. It is also found that the introduction of positive charges causes not only the change in the sign of γ but also a significant enhancement of the magnitude. Judging from the present results, the extended dendrimers involving linking N atoms are expected to exhibit significantly large γ values due to an extension of π-conjugation, and the introduction of positive charges is further predicted to cause drastic changes both in sign and magnitude of their γ values.

1. Introduction

The nonlinear optical (NLO) properties for organic compounds have been actively studied because of their large nonlinearity and fast responses, which originate in π-electron conjugation of organic compounds.[1−4] One of the recent topics in this field is the NLO properties of dendrimers.[5,6] Dendrimer is a new class of polymeric systems, the structures of which are often referred to as "fractal (Caley-tree) structures" and are characterized by a large number of terminal groups originating in a focal point with at least one branch at each repeat unit. It is known that dendrimers exhibit several attractive chemical and physical functions, e.g., high light-harvesting property,[7−9] encapsulating property as a unimolecular container molecule,[10] and catalytic property with high turnover.[11] For example, phenylacetylene dendrimers exhibit high light-harvesting properties, which are predicted to be caused by the efficient exciton migration from the periphery to the core region. Such efficient exciton migration has been investigated experimentally and theoretically,[12−15] and the origin of such behavior has been found to be in the dendritic structure, in which the length of π-conjugation in linear-leg regions composed of diphenylacetylene units increases from the periphery to the core, and the π-conjugation is decoupled well at the *meta*-branching points (benzene-rings). The NLO properties of such phenylacetylene dendrimers have been analyzed using molecular orbital (MO) calculations,[16] and the spatial contributions to the second hyperpolarizabilities (γ), which are the microscopic origin of third-order NLO properties, are well localized in linear-leg regions though the contributions are somewhat enhanced as compared to those of isolated linear-legs by the remaining π-conjugation via *meta*-branching points. Speculated from these results, the NLO properties for other types of dendrimers with π-conjugation extended over the whole region are expected to be enhanced significantly. For example, the γ values for dendrimers composed of π-conjugated phenylenevinylenes, mutually linked by nitrogen (N) atoms, are interesting since the lone-pair π-electrons on the linking N atoms are expected to contribute to the extended π-conjugation via N atoms. As one of the simplest models for such extended dendrimers, we consider 1,4-phenylendiamine (PDA) (see Figure 1a) and 4,4′-diaminodiphenylamine (DADPA) (Figure 1b) using the ab initio MO calculations.



(a) PDA (b) DADPA

Figure 1. Structures of 1,4-phenylendiamine (PDA) (a) and 4,4′-diaminodiphenylamine (DADPA) (b).

On the other hand, the introduction of charged defects is found to dramatically enhance the magnitude of γ and to even change the sign of γ in some cases.[17−19] In this study, therefore, we also investigate the effects of introducing charged defects on the γ using dicationic PDA and DADPA models. The features of γ for these systems are elucidated in view of the spatial contribution of electrons using the γ density analysis.[20] On the basis of the present results, we discuss the NLO properties of extended dendrimers involving linking N atoms.

2. Symmetric Resonance Structures with Invertible Polarization (SRIP)

We here briefly explain our structure−property relation in the third-order NLO properties for molecular systems. The

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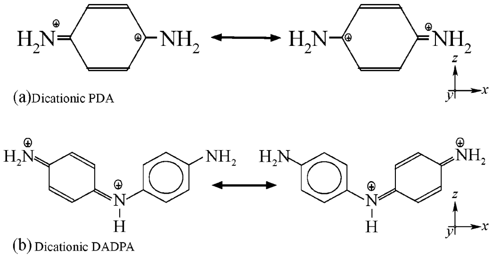


Figure 2. Symmetric resonance structures with invertible polarization (SRIP) of dicationic PDA (a) and DADPA (b).

perturbative formula for static γ can be partitioned into three types of contributions as follows:[17]

$$\gamma^{(\mathrm{I})+(\mathrm{II})+(\mathrm{III})} = \gamma^{(\mathrm{I})} + \gamma^{(\mathrm{II})} + \gamma^{(\mathrm{III})} = \sum_{n=1} \frac{(\mu_{n0})^2(\mu_{nn})^2}{E_{n0}^{\ 3}} - \sum_{n=1} \frac{(\mu_{n0})^4}{E_{n0}^{\ 3}} + \sum_{\substack{m,n=1\\(m\neq n)}} \frac{(\mu_{n0})^2(\mu_{mn})^2}{E_{n0}^{\ 2}\,E_{m0}} \quad (1)$$

Here, μ_{n0} is the transition moment between the ground and the nth excited states, μ_{mn} is the transition moment between the mth and the nth excited states, μ_{nn} is the difference of dipole moments between the ground and the nth excited states and E_{n0} is the transition energy given by ($E_n - E_0$). From these equations, apparently, the contributions of $\gamma^{(\mathrm{I})}$and $\gamma^{(\mathrm{III})}$ are positive in sign, whereas the contribution of $\gamma^{(\mathrm{II})}$ is negative. On the basis of this partitioning, we have proposed a structure–property relation in γ.[17,18] We here particularly consider a case, i.e., $|\gamma^{(\mathrm{I})}| = 0$, $|\gamma^{(\mathrm{II})}| > |\gamma^{(\mathrm{III})}|$ ($\gamma < 0$), in which the compounds are symmetric ($\mu_{nn} = 0$) and exhibit strong virtual excitation between the ground and the first excited states ($|\mu_{0n}| > |\mu_{mn}|$). From this condition, the symmetric systems with large polarization are predicted to exhibit negative γ, which is rare in general for conventional π-conjugated molecules, but important for the application in NLO. Namely, a system with large contribution of symmetric resonance structures with invertible polarization, i.e., SRIP, satisfies our criteria for the system to have a negative γ.

Figure 2 shows SRIP for dicationic states of PDA and DADPA. Since the displacement of charges between resonance structures tends to occur in the longitudinal (x) direction, longitudinal γ components (γ_{xxxx}) should be primarily affected by SRIP contributions in both systems. As shown in Figure 2a, the displacement of charges in SRIP for PDA is small, the positive and negative contributions to γ_{xxxx} are predicted to cancel with each other, so that the magnitude of γ_{xxxx} for PDA is predicted to become small. On the other hand, DADPA is expected to have large SRIP contributions because of their large displacement of charges, so that the dicationic DADPA is predicted to have a negative γ_{xxxx} with a large magnitude.

3. Calculation Methods

Each geometry of PDA and DADPA is optimized by the Møller–Plesset second-order perturbation (MP2) method using the 6-31G** basis set under the condition of C_{2v} planar structures. In the calculation of NLO properties for PDA and DADPA, the 6-31G and 6-31G+d, which are augmented with diffuse d function on carbon (C) and nitrogen (N) atoms, are used. The augmentation of diffuse functions is known to be necessary in general for obtaining quantitative NLO properties of π-conjugated systems.[21] The orbital exponents for augmented d function in 6-31G+d are chosen as 0.0523 for C and 0.0582 for N by the even-tempered method.[22] Since the electron correlation effects on γ are known to be large for SRIP systems,[4,18,22] we apply the nth-order Møller–Plesset perturbation (MPn), coupled-cluster (CC), and quadratic configuration-interaction (QCI) methods to the calculation of γ. All of the ab initio MO calculations are performed using the Gaussian 98 program package.[23]

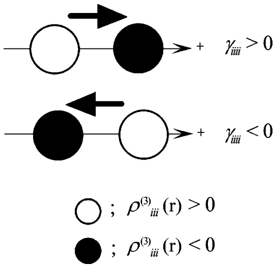


Figure 3. Schematic diagram of the second hyperpolarizability (γ_{iiii}) densities $\rho^{(3)}_{iii}(\mathbf{r})$. White and black circles represent positive and negative values of $\rho^{(3)}_{iii}(\mathbf{r})$, respectively. The size of circle represents the magnitude of $\rho^{(3)}_{iii}(\mathbf{r})$ and the arrow shows the sign of γ_{iiii} determined by the relative spatial configuration between these two $\rho^{(3)}_{iii}(\mathbf{r})$ values.

The γ value is numerically calculated by the fourth-order differentiation of the total energy E with respect to the applied field $\mathbf{F}$:

$$\gamma_{ijkl} = -\frac{1}{3!}\frac{\partial^4 E(\mathbf{F})}{\partial F^i \partial F^j \partial F^k \partial F^l}\Big|_{F=0} \quad (2)$$

Here, $E(\mathbf{F})$ indicates the total energy in the presence of the applied field $\mathbf{F}$. To avoid numerical errors, we try several field strengths from 0.001 to 0.004 au as the minimum finite field and adopt a numerically stable γ.

We briefly explain the hyperpolarizability density analysis of the static γ in the FF approach.[24] The charge density function $\rho(\mathbf{r}, \mathbf{F})$ can be expanded in powers of field $\mathbf{F}$ as

$$\rho(\mathbf{r}, \mathbf{F}) = \rho^{(0)}(\mathbf{r}) + \sum_j \rho_j^{(1)}(\mathbf{r})F^j + \frac{1}{2!}\sum_{jk}\rho_{jk}^{(2)}(\mathbf{r})F^jF^k + \frac{1}{3!}\sum_{jkl}\rho_{jkl}^{(3)}(\mathbf{r})F^jF^kF^l + \ldots \quad (3)$$

From this equation and the expansion formula of the dipole moment in powers of the field, the static γ can be expressed by[20]

$$\gamma_{ijkl} = -\frac{1}{3!}\int r^i \rho_{jkl}^{(3)}(\mathbf{r})\,\mathrm{d}\mathbf{r} \quad (4)$$

where

$$\rho_{jkl}^{(3)}(\mathbf{r}) = \frac{\partial^3 \rho}{\partial F^j \partial F^k \partial F^l}\Big|_{F=0} \quad (5)$$

This third-order derivative of the electron density with respect to the applied electric fields is referred to as the second hyperpolarizability (γ) density ($\rho^{(3)}_{iii}(\mathbf{r})$).

To explain the analysis procedure using the hyperpolarizability densities, let us consider a pair of localized $\rho^{(3)}_{iii}(\mathbf{r})$ shown in Figure 3. The positive sign of the $\rho^{(3)}_{iii}(\mathbf{r})$ implies that the second derivative of the charge density increases with the increase in the field. The arrow from a positive to a negative $\rho^{(3)}_{iii}(\mathbf{r})$ shows the sign of the contribution determined by the relative spatial configuration between the two $\rho^{(3)}_{iii}(\mathbf{r})$. Namely, the sign of the contribution becomes positive when the direction of the arrow coincides with the positive direction of the

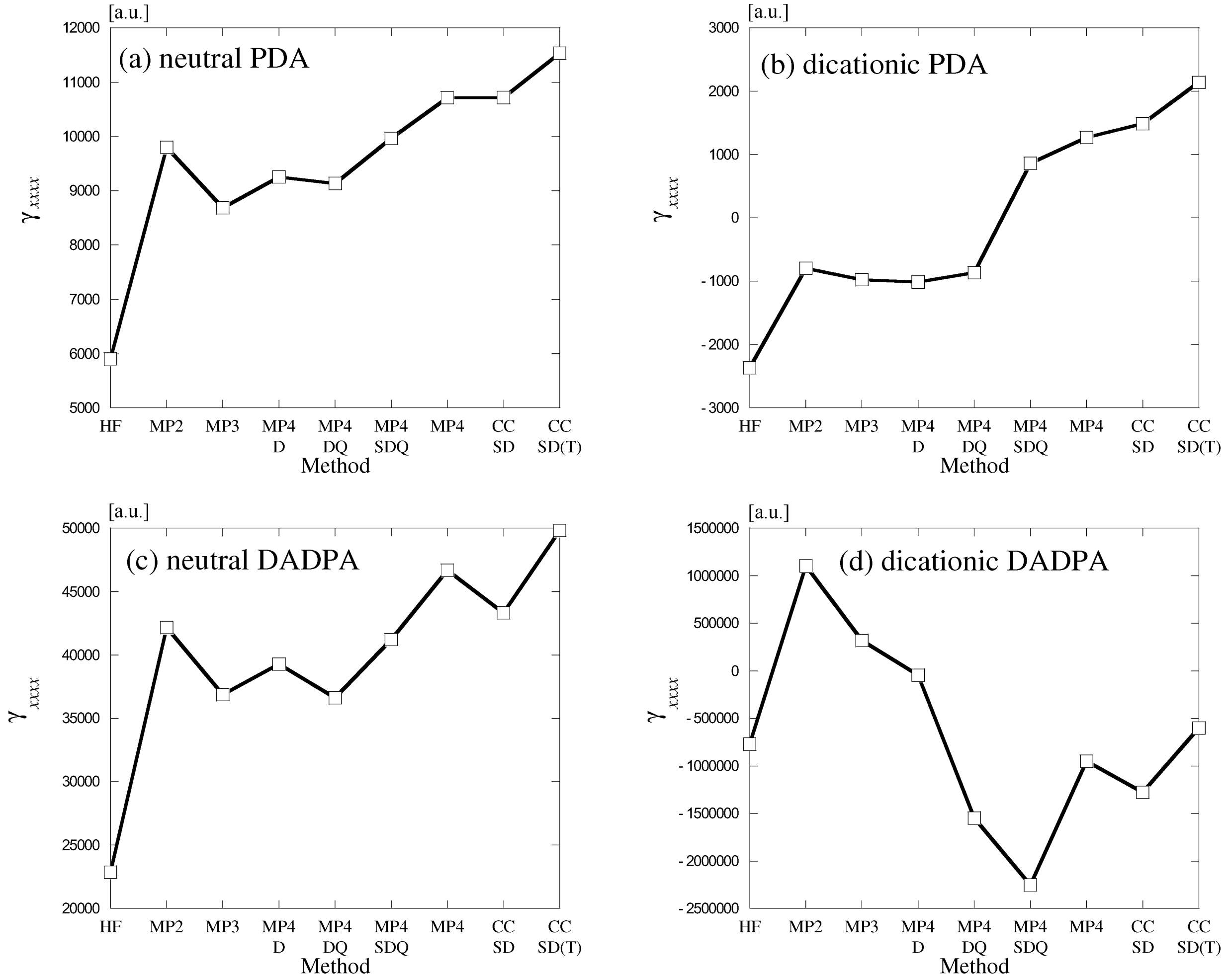


Figure 4. Variations in the γ_{xxxx} of neutral PDA (a), dicationic PDA (b), neutral DADPA (c), and dicationic DADPA (d). The γ_{xxxx} values for PDA and DADPA are calculated using 6-31G+d and 6-31G basis sets, respectively.

TABLE 1: G Values [a.u.] of Neutral and Dicationic PDA and DADPA Calculated by the HF and MP2 Methods with 6-31G and 6-31G+d Basis Sets

			neutral			dicationic		
system	method	basis set	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}
PDA	HF	6-31G	2150	10	180	−3110	10	440
		6-31G+d	6000	1980	1650	−2450	550	670
	MP2	6-31G	3240	10	190	−1560	10	600
		6-31G+d	9910	3010	2330	−880	640	930
DADPA	HF	6-31G	23100	20	430	−771100	20	1230
		6-31G+d	30400	2840	3150	−848600	1330	1720
	MP2	6-31G	42400	20	470	1091600	20	1180
		6-31G+d	57400	3920	4570	1247300	1640	2460

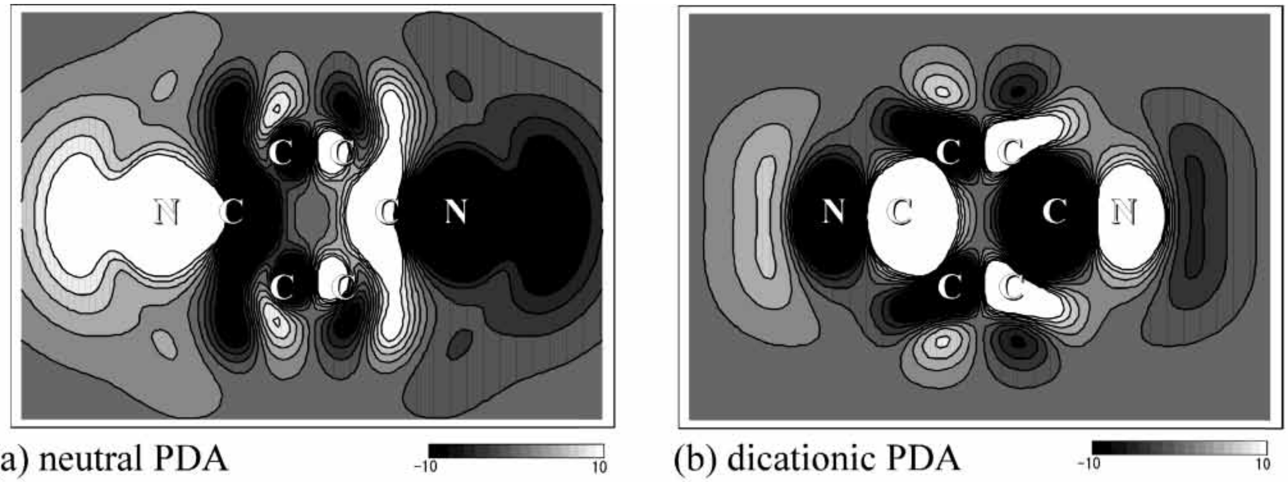
coordinate system. The contribution determined by the $\rho^{(3)}_{iii}(\mathbf{r})$ of the two points is more significant when their distance is larger. We evaluated charge densities at three-dimensional grid points using the Gaussian 98 program package.[23]

4. Results and Discussion

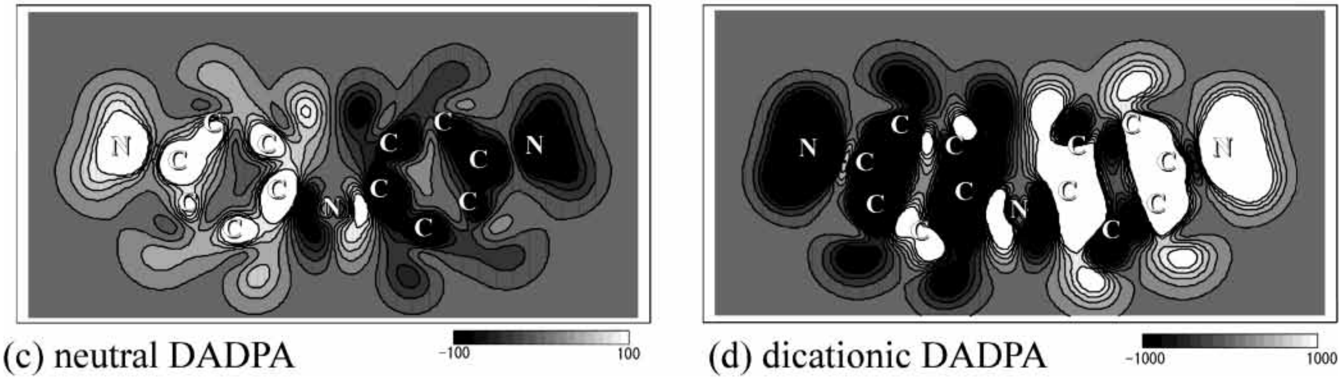
4.1. Basis Set and Electron Correlation Dependencies for γ Values of PDA and DADPA. Table 1 gives the calculated values of γ_{xxxx}, γ_{yyyy}, and γ_{zzzz} for PDA and DADPA in neutral and dicationic states at the HF and MP2 levels. Since the magnitude of the γ_{xxxx} component ($|\gamma_{xxxx}|$) is shown to be dominant in both systems, the γ_{xxxx} value could be used for examining the relation among the features of the γ value and SRIP contributions for these quasi-one-dimensional systems though the spatially averaged γ values, $\langle\gamma\rangle$, have to be investigated for two and/or three-dimensional dendrimers. It is noted that the structure−property relation extracted from the γ_{xxxx} for these model systems will be also useful for the analysis and understanding of the essential mechanism of characterizing γ for larger two and three-dimensional dendrimers. We therefore concentrate our attention to γ_{xxxx} value in the following discussion.

For PDA, an augmentation of diffuse d function is found to enhance about three times the γ_{xxxx} values of neutral PDA at the HF and MP2 levels, whereas the γ_{xxxx} value of dicationic PDA is shown to be negative in sign and the augmentation of diffuse function significantly reduces the $|\gamma_{xxxx}|$ at the HF level. Therefore, the augmentation effect is presumed to give a positive contribution to γ_{xxxx} of PDA. In contrast, the augmentation effect is found to only slightly increase the γ_{xxxx} values of neutral and dicationic DADPA. Judging from the basis set dependencies and the fact that the DADPA involves two units of PDA (see Figure 1), the basis set dependency is predicted to be less significant as the size of molecule enlarges. This prediction agrees with the previous results[21] on the basis set dependency of NLO properties for π-conjugated long-chain systems. Therefore, 6-31G and 6-31G+d basis sets are employed for the calculations of γ_{xxxx} values of PDA and DADPA, respectively.

Figure 4 shows the electron correlation dependencies of γ_{xxxx} values for PDA and DADPA in neutral and dicationic states. The electron correlation effects are shown to be extremely different between neutral and dicationic states of both molecules. For the neutral states of PDA (see Figure 4a) and DADPA (see



(a) neutral PDA (b) dicationic PDA



(c) neutral DADPA (d) dicationic DADPA

Figure 5. Contour plots of γ density distributions on the plane 1.0 au above molecular plane for $\rho^{(3)}_{xxx}(\mathbf{r})$ of neutral PDA [$\gamma_{xxxx} = 11\,400$ au] (a), dicationic PDA [$\gamma_{xxxx} = 1900$ au] (b), neutral DADPA [$\gamma_{xxxx} = 47\,000$ au] (c), and dicationic DADPA [$\gamma_{xxxx} = -1\,191\,000$ au] (d). The γ_{xxxx} values of PDA and DADPA and their γ densities are calculated by using QCISD method with 6-31G+d and 6-31G basis sets, respectively. The range of each contour is shown below each density map.

Figure 4c), the results calculated by the CCSD(T) method, which is the highest electron correlation method in this study, are found to be well reproduced by the MP2 method. For dicationic PDA, however, the electron correlation correction at the MP2 level is about one-third of that at the CCSD(T) level (see Figure 4b). It is also shown that the sign of γ_{xxxx} (negative) for PDA calculated by the HF and MP2 methods is changed into positive beyond the MP4DQ level. As shown in Figure 4d, the electron correlation effect on γ_{xxxx} of dicationic DADPA is rather complicated. It is shown that the γ_{xxxx} values are negative in sign beyond the MP4D levels though the MP2 methods provide significantly large positive γ_{xxxx} value (see Table 1). Judging from the difference in γ_{xxxx} values between the MP4D and MP4DQ methods, the higher-order quadruple excitation effect on the γ_{xxxx} value is predicted to give a significant negative contribution. Therefore, the converged γ_{xxxx} value of dicationic DADPA is inferred to be negative in sign though the γ_{xxxx} value is still unconverged well even at the CCSD(T) level.

As a result, all of the systems except for the dicationic DADPA are predicted to provide positive γ_{xxxx} values. These results are found to be in good agreement with our prediction based on SRIP discussed in section 2. It is also found from the CCSD(T) results that the γ_{xxxx} value (49 800 au) of neutral DADPA is about four times as large as that (11500 au) of neutral PDA. Since the γ_{xxxx} value of neutral DADPA is calculated using the 6-31G basis set, the γ_{xxxx} value using the 6-31G+d basis set would be further enhanced. Such nonlinear enhancement of γ_{xxxx} in neutral DADPA as compared to that in PDA is ascribed to be the extension of π-conjugation in the longitudinal direction via a linking N atom of DADPA. The introduction of positive charges into these π-conjugated systems is predicted to increase the negative contribution ($\gamma^{(\mathrm{II})}$, see eq 1) because such a system tends to have large SRIP contributions. Actually, the dicationic DADPA at the CCSD(T) level exhibits a large negative γ_{xxxx} value ($-600\,500$ au) though the dicationic PDA retains slightly positive γ_{xxxx} value (2140 au) due to the small SRIP contribution (see section 2). It is also found from the CCSD(T) results that the extraordinary enhancement (about 12 times) of $|\gamma_{xxxx}|$ in dicationic DADPA (600 500 au) occurs as compared to $|\gamma_{xxxx}|$ of neutral DADPA (49 800 au) by introducing positive charges.

4.2. Spatial Contributions to γ by the Hyperpolarizability Density Analysis. Figure 5 shows the distributions of $\rho^{(3)}_{xxx}$ (γ_{xxxx} densities) on the plane 1.0 au located above the molecular plane for each system. All γ_{xxxx} densities for PDA and DADPA are calculated by the QCISD method, which is known to well reproduce the results by the CCSD method. For PDA, the lone-pairs of both-end N atoms are shown to provide dominant positive contributions to γ_{xxxx} in the neutral state, whereas in the dicationic state, those contributions are shown to be negative in sign. In the dicationic PDA, however, the magnitudes of the negative contributions are shown to be slightly smaller than those of positive contributions in a benzene region, so that the significant cancellation between positive and negative contributions occurs, giving slightly positive γ_{xxxx} of dicationic PDA. On the other hand, the γ_{xxxx} densities for neutral and dicationic DADPA are shown to be primarily distributed on both aminobenzene regions with mutually opposite signs. Namely, the large positive (negative) contributions between both aminobenzene units are detected for neutral (dicationic) DADPA. In both states, the contributions are found to be caused by the virtual

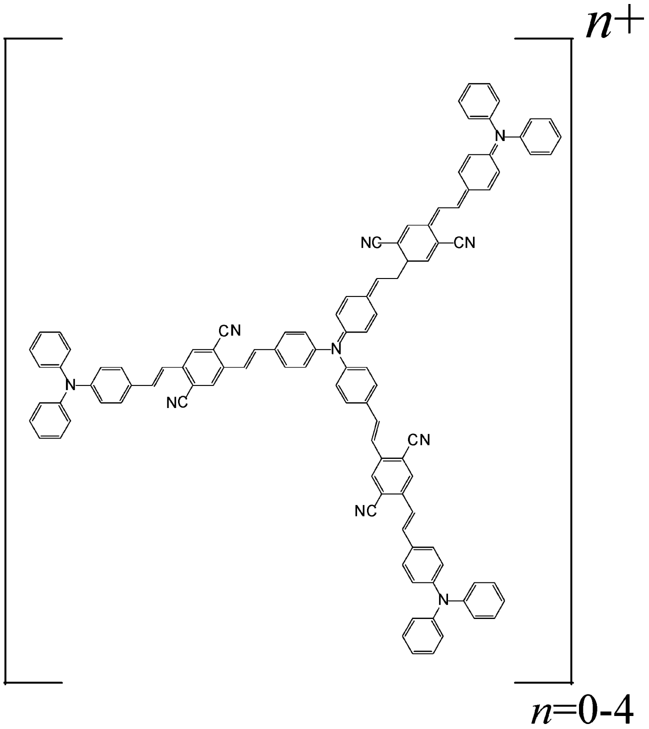


Figure 6. Example of extended π-conjugated systems, in which three π-conjugated units (phenylene vinylene derivatives) are linked mutually by an N atom.

charge transfer (CT) between both aminobenzene units via the central linking N atom. This is predicted to originate in the extension of π-conjugation over both aminobenzene units via a linking N atom. Such distinct negative contribution between both aminobenzene units corresponds to the large SRIP contribution in this molecule (see Figure 2b).

5. Concluding Remarks

Two kinds of drastic changes on the second hyperpolarizabilities (γ) of dendritic π-conjugated systems were predicted. One is a remarkable enhancement of γ in neutral DADPA, the feature of which is caused by the connection of two π-conjugated units via a central N atom. The extension of π-conjugation over both end units via the lone pair on the central N atom was found to cause such nonlinear enhancement in γ_{xxxx} values of DADPA. The other is caused by the introduction of positive charges to the π-conjugated systems. It was shown that the large SRIP contribution for dicationic DADPA gives a negative sign of γ_{xxxx} and significantly enhances the magnitude of γ_{xxxx}. Such large SRIP contribution was predicted to be related to the lone pair on the central N atom that links the π-conjugated units. On the basis of the present results, an extremely large enhancement in γ values is expected for extended π-conjugated dendrimers including linking N atoms (see Figure 6a for example). Actually, remarkable two photon absorption, which is described by the imaginary part of $\gamma(-\omega;\omega,-\omega,\omega)$, has been reported in the neutral ($n = 0$) molecule shown in Figure 6.[25] Judging from the effect of introducing charged defects into the extended π-conjugated systems, poly-cationic extended π-conjugated dendrimers (see Figure 6 for example) could exhibit a dramatic change in the magnitude and sign of γ as compared to their neutral species. Such a considerable variation of γ values depending on the charged states will be useful for the realization of novel, i.e., controllable, nano-structured NLO systems.

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