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Diradicalology in Third-Order Nonlinear Optical Systems: Second Hyperpolarizabilities of Acetylene-Linked Phenalenyl-Based Superpolyenes

Masayoshi Nakano,^{*,[a]} Ryohei Kishi,^[a] Hitoshi Fukui,^[a] Takuya Minami,^[a] Kyohei Yoneda,^[a] Shu Minamide,^[a] Yudai Inoue,^[a] Taishi Yamada,^[a] Soichi Ito,^[a] Shabbir Muhammad,^[a] Yasuteru Shigeta,^[a] Takashi Kubo,^[b] and Benoît Champagne^[c]

From the viewpoint of “diradical character,” referred to as “diradicalology,” we investigate the second hyperpolarizability γ —the molecular third-order nonlinear optical (NLO) property—of one-dimensional supermolecular systems composed of acetylene-linked phenalenyl/pyrene rings using long-range corrected spin-unrestricted density functional theory. It turns out that the pyrene-based superpolyenes (Py- n) behave like closed-shell systems, whereas phenalenyl-based superpolyenes (Ph1- n and Ph2- n) have different diradical characters depending on the linked form, that is, Ph1- n and Ph2- n have intermediate and pure diradical characters,

respectively. In comparison with Py- n and Ph2- n , the longitudinal γ of Ph1- n is significantly larger, and it displays larger enhancement as a function of system size. Substitutions to the terminal rings by donor (NH₂) and acceptor (NO₂) groups further enhance γ in Ph1- n , more than in Ph2- n and Py- n . These results are in agreement with the structure–property relationships derived for open-shell NLO systems with symmetric and asymmetric charge distributions (Nakano et al., *J. Chem. Phys.* 2010, 133, 154302). © 2012 Wiley Periodicals, Inc.

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Introduction

Recently, several polycyclic aromatic hydrocarbons (PAHs) including graphenes^[1,2] have attracted much attention from the viewpoint of their unique electronic structures, that is, open-shell singlet ground states characterized by intermediate and strong antiparallel spin correlation, or by the intermediate and large fractional occupation numbers n ($0 < n \leq 1$) in the lowest unoccupied natural orbitals (LUNOs).^[3] In other words, such systems belong to the intermediate/strong electron correlation regime, which are well illustrated by the electronic structures of the singlet H₂ in the intermediate/complete dissociation region.^[4] These correlated electronic structures generally tend to be sensitive to external chemical and physical perturbations, for example, slight structural changes, donor/acceptor (DA) substitutions, intermolecular interactions, spin/charge state changes, solvent effects, and the application of electromagnetic fields. Moreover, such correlation features are observed not only in the ground state but also in the excited states, because these states closely interact with each other, which tunes the relative fractions of ionic and covalent (diradical) contributions.^[5,6] Namely, the chemical structures, reactivities, and physicochemical properties of the ground and excited states are expected to be strongly influenced by slight external perturbations as compared to the closed-shell systems, that is, weak correlated systems.^[7–9] So, the description and the control of the physicochemical properties often refer to the open-shell character, which can be quantified by the radical character. In these systems, the latter takes the form of the diradical^[10–13] or multiradical^[3,11] character. We could thus propose the “diradicalology” concept, which allows us to

explore the origins and/or to create/control the electron-correlation-driven physicochemical phenomena as a function of the diradical characters in the broad fields of physics, chemistry, and biology.

In this study, we investigate the third-order nonlinear optical (NLO) properties—at the molecular level, the second hyperpolarizability (γ)—of open-shell singlet systems from the viewpoint of diradicalology. It has been theoretically found that the NLO properties of such systems are strongly correlated with their diradical characters and that molecular systems with intermediate diradical characters exhibit significant enhancements of γ as well as giant field-induced enhancements as compared to conventional closed-shell systems.^[4,6,14–17] The validity of this structure–property relationship has been computationally confirmed using various open-shell singlet models and real compounds including hydrogen atom chains,^[6,14,18] *p*-quinodimethane model,^[14] diphenalenyl diradicaloids,^[19,20] graphene nanoflakes,^[21–23] and transition metal compounds.^[24,25] These results have been also supported by recent experimental data

[a] M. Nakano, R. Kishi, H. Fukui, T. Minami, K. Yoneda, S. Minamide, Y. Inoue, T. Yamada, S. Ito, S. Muhammad, Y. Shigeta
Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
E-mail: mnaka@cheng.es.osaka-u.ac.jp

[b] T. Kubo
Department of Chemistry, Graduate School of Science, Osaka University
Toyonaka, Osaka 560-0043, Japan

[c] B. Champagne
Laboratoire de Chimie Théorique (LCT), Facultés Universitaires Notre-Dame de la Paix (FUNDP), Rue de Bruxelles, 61, Namur B-5000, Belgium

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on two-photon absorption^[26] and third harmonic generation,^[27] and they have stimulated other investigations on linear and NLO properties^[28–39] of multiradical compounds as well as their vibrational signatures.^[40,41] In previous studies,^[20,42,43] spin-unrestricted hybrid density functional theory (UDFT) calculations have shown that supermolecular and supramolecular multiradical systems composed of phenalenyl units are promising NLO systems, because their properties can be controlled by adjusting the architectures, the diradical characters, and the charge states. In this study, we investigate a different series of open-shell ‘superpolyene’ systems composed of acetylene-linked phenalenyl radicals, that is, super-ethylene and super-butadiene, with a focus on the effects of link pattern and of DA substitutions, to clarify the relationship between the chemical structures, the diradical characters, and γ .^[16,17]

Theoretical and Computational Details

Geometrical structures and diradical characters

Figure 1 shows the structures of acetylene-linked superpolyenes composed of pyrene rings, Py- n (a, $R_1=R_2=H$), phenalenyl rings, Ph1- n (b, $R_1=R_2=H$) and Ph2- n (c, $R_1=R_2=H$), as well as their donor (NH_2)/acceptor (NO_2) disubstituted analogs,

DA-Py- n (a, $R_1=NH_2$, $R_2=NO_2$), DA-Ph1- n (b, $R_1=NH_2$, $R_2=NO_2$), and DA-Ph2- n (c, $R_1=NH_2$, $R_2=NO_2$), where n indicates the number of pyrene/phenalenyl rings. There is a difference in the anchoring position of the acetylene linker on the phenalenyl ring between Ph1- n and Ph2- n . It has been predicted that Ph1-2 has an intermediate diradical character, whereas Ph2-2 has a pure diradical character.^[20] All systems are neutral singlet ground states, and $n = 2$ (super-ethylene) and 4 (super-butadiene) are considered. The spin-unrestricted (U)/spin-restricted (R) B3LYP exchange-correlation functional with the 6-31G* basis set was adopted for the geometry optimizations, because it reproduces the experimental structures of conjugated diradical systems.^[44,45] The molecules were constrained to be planar (in the x - z plane) with the exception of DA-Ph1- n , which is almost planar but adopts C_1 symmetry. This planarity leads to high symmetry for the nonsubstituted systems, that is, Py-2 (C_{2h}), Py-4 (C_{2h}), Ph1-2 (C_{2h}), Ph2-2 (D_{2h}), and Ph2-4 (C_{2h}), whereas the DA-substituted systems belong to the C_1 symmetry. The molecules are oriented, so that the line connecting the carbon atoms of the middle acetylene linker forms an angle of 30° with the longitudinal (z) axis. Following Ref. [43], it is here noteworthy to examine the lengths of the acetylene linkers ($C-C\equiv C-C$), referred to as linker bonds, for the nonsubstituted systems from the viewpoint of the bond length alternation (BLA), a characteristic of regular polyenes. These lengths are: 4.067 Å (Py-2), 4.064 Å (end, Py-4), 4.064 Å (center, Py-4), 4.000 Å (Ph1-2), 4.014 Å (end, Ph1-4), 4.033 Å (center, Ph1-4), 4.057 Å (Ph2-2), 4.067 Å (end, Ph2-4), and 4.067 Å (center, Ph2-4). So, (i) the linker-bond lengths of Ph1- n are smaller than those of Py- n and Ph2- n , (ii) a slight BLA is observed between the end and the center linker bonds of Ph1-4, and (iii) the linker-bond lengths of Py-4 and Ph2-4 are almost the same, and no alternation is observed. Like in similar phenalenyl/pyrene-based superpolyenes,^[43] this suggests that the acetylene-linker bonds of singlet Ph1- n somewhat mimic the behavior of carbon-carbon bonds in regular polyenes, though the linker-bond interactions are much weaker, whereas the linker bonds of Ph2- n and Py- n would correspond to the single carbon-carbon bonds of saturated hydrocarbons. Moreover, the DA substitution hardly affects the linker-bond lengths in Py- n and Ph2- n , whereas in Ph1- n it increases slightly the BLA, that is, 3.988 Å (DA-Ph1-2), 3.989 Å (end, DA-Ph1-4), and 4.041 Å (center, DA-Ph1-4) with respect to Ph1-4.

These multiradical systems are described by their successive diradical characters (y_i), defined as the occupation numbers of the LUNO + i , where $i = 0, 1, \dots$, obtained using a spin-unrestricted single-determinant scheme:^[3]

$$y_i = n_{\text{LUNO}+i} = 2 - n_{\text{HONO}-i}, \quad (1)$$

where the second equality [$n_{\text{HONO}-i}$ is the occupation number of the highest occupied natural orbital (HONO) - i] is satisfied within single-determinant schemes. In such a case, the y_i value means the probability ($0 \leq y_i \leq 1$) for the electron of being unpaired in orbital LUNO + i (HONO - i), for example, $y_i = 1$ represents a pure diradical (singly occupied LUNO + i and HONO - i), $y_i = 0$ corresponds to a closed-shell system and a

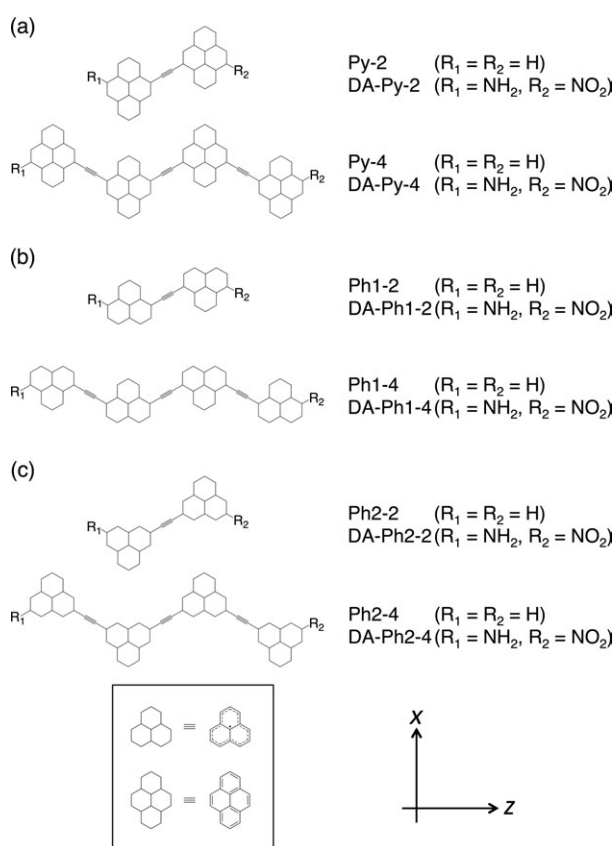


Figure 1. Structures of the singlet superpolyene systems composed of acetylene-linked pyrene [Py- n ($n = 2, 4$) (a, $R_1=R_2=H$)] and phenalenyl [Ph1- n ($n = 2, 4$) (b, $R_1=R_2=H$) and Ph2- n ($n = 2, 4$) (c, $R_1=R_2=H$)] rings as well as of donor (NH_2)-acceptor (NO_2)-substituted analogs [DA-Py- n ($n = 2, 4$) (a, $R_1=NH_2$, $R_2=NO_2$), DA-Ph1- n ($n = 2, 4$) (b, $R_1=NH_2$, $R_2=NO_2$), and DA-Ph2- n ($n = 2, 4$) (c, $R_1=NH_2$, $R_2=NO_2$)]. Cartesian axes are also shown.

doubly occupied HONO – i , and $0 < y_i < 1$ describes an intermediate diradical character. Equation (1) was evaluated using the LC-UBLYP/6-31G* method with a range separating parameter $\mu = 0.33$, which is known to provide reliable excitation energies, transition properties, and response properties of closed-shell molecular systems^[46–48] as well as response properties of open-shell molecular systems.^[49,50] As the UDFT with an appropriate functional is also found to well reproduce the diradical characters obtained by the highly correlated, for example, spin-unrestricted coupled-cluster singles and doubles (UCCSD), method, we do not evaluate spin-projected diradical characters.

Second hyperpolarizability and hyperpolarizability density analysis

The longitudinal component of γ , γ_{zzzz} , was calculated by adopting the finite-field approach,^[51] which consists in the fourth-order differentiation of the energy^[20] or the second-order differentiation of the polarizability calculated by the coupled-perturbed Kohn–Sham method^[52] with respect to the electric field (F). The LC-UBLYP exchange–correlation functional with $\mu = 0.33$ was used, because it semiquantitatively reproduces the γ of several open-shell molecules calculated with the highly correlated spin-unrestricted coupled cluster methods.^[49,50] Although for small compounds, the use of extended basis sets including several sets of polarization and diffuse functions is required, even for obtaining qualitative γ values,^[53–60] the standard 6-31G* basis set was adopted since such basis set is expected to provide semiquantitative description of, at least, the longitudinal and dominant γ tensor component in extended π -conjugated systems.^[61] Indeed, this choice was substantiated by previous results that the 6-31G* basis set reproduces within 10% the γ value of *s*-indaceno[1,2,3-*cd*;5,6,7-*c'd'*]diphenylene (IDPL), calculated using the 6-31G* + diffuse p ($\zeta = 0.0523$) basis set,^[19] which is known to reproduce the γ for several relatively large open-shell systems at the highly correlated level of approximation using more extended basis sets.^[55]

Moreover, we performed the hyperpolarizability density analysis^[62] to clarify the spatial electronic contributions to γ . From the expansions of the charge density function $\rho(\mathbf{r}, F)$ and the dipole moment in a power series of the applied electric field F , the static γ reads

$$\gamma = -\frac{1}{3!} \int r \rho^{(3)}(\mathbf{r}) d^3\mathbf{r}, \quad (2)$$

where

$$\rho^{(3)}(\mathbf{r}) = \left. \frac{\partial^3 \rho}{\partial F^3} \right|_{F=0} \quad (3)$$

Here, r represents the z -component of the electron coordinate. This third-order derivative of the electron density with respect to the applied electric fields, $\rho^{(3)}(\mathbf{r})$, is referred to as the γ density. Positive/negative $\rho^{(3)}(\mathbf{r})$ values multiplied by F^3 correspond therefore to the third-order field-induced electron density variations, giving rise to the third-order contribution to the dipole moment in the direction from positive to negative γ

density. The γ densities are calculated for a grid of points using a numerical third-order differentiation formula. All calculations were performed using the Gaussian 09 program package.^[63]

Results and Discussion

Diradical character dependences of γ in unsubstituted superpolyenes

In their singlet ground state, the Py- n systems are closed shell as evidenced by the zero values of y_0 and y_1 (Table 1), which enables Py- n to play the role of closed-shell references. The y_0

Table 1. Diradical characters (y_0 , y_1)^a and γ values for closed-shell (Py- n and DA-Py- n) and open-shell (Ph1- n , Ph2- n , DA-Ph1- n , and DA-Ph2- n) superpolyene systems in the singlet spin states in comparison with those of Pyn and Phn ($n = 2, 4$) from Ref. [43].

| System | y_0 | y_1 | γ ($\times 10^3$ a.u.) |
|---------------------|--------|--------|--------------------------------|
| Py-2 | 0.0 | 0.0 | 147 |
| Py-4 | 0.0 | 0.0 | 727 |
| Ph1-2 | 0.5698 | 0.0411 | 1740 |
| Ph1-4 | 0.7546 | 0.5433 | 21,000 |
| Ph2-2 | 0.9987 | 0.0397 | 110 |
| Ph2-4 | 0.9992 | 0.9978 | 572 |
| DA-Py-2 | 0.0 | 0.0 | 170 |
| DA-Py-4 | 0.0 | 0.0 | 772 |
| DA-Ph1-2 | 0.5413 | 0.0426 | 5750 |
| DA-Ph1-4 | 0.6609 | 0.4994 | 34,000 |
| DA-Ph2-2 | 0.9986 | 0.0408 | 150 |
| DA-Ph2-4 | 0.9992 | 0.9978 | 627 |
| Py2 ^[43] | 0.570 | 0.041 | 500 |
| Py4 ^[43] | 0.752 | 0.493 | 5250 |
| Ph2 ^[43] | 0.0 | 0.0 | 120 |
| Ph4 ^[43] | 0.0 | 0.0 | 460 |

[a] The y_0 and y_1 values are obtained from the occupation numbers of LUNO and LUNO + 1, respectively, calculated by the LC-(U)BLYP/6-31G* method.

values of Ph1- n ($n = 2, 4$) lie in the intermediate region and increases with the number of monomers [Ph1-2 ($y_0 = 0.570$) and Ph1-4 ($y_0 = 0.755$)]. The y_1 value of Ph1-2 is negligible, whereas that of Ph1-4 exhibits an intermediate value ($y_1 = 0.543$). So, Ph1-2 and Ph1-4 are regarded as intermediate diradical and tetraradical systems, respectively. In contrast, y_0 of Ph2-2 and (y_0 , y_1) of Ph2-4 are equal to ~ 1 , and these systems are pure diradical and tetraradical systems, respectively. These facts on Py- n and Ph1- n are similar to those between Pyn and Phn in Ref. [43] (see also Table 1), the feature of which is understood by the similarity of their topologies.

The intermediate diradical characters of the Ph1- n systems imply that the radicals on each phenalenyl ring interact with each other with intermediate strength in an antiferromagnetic manner through the acetylene π -conjugated linkers, which results in the delocalization of the radical spins over the whole system. In contrast, the strong correlation between the radical electrons and their antiferromagnetic coupling leads to the pure diradical character of the Ph2- n systems. This is exemplified by the Mulliken spin density maps (Fig. 2). The dominant positive (up) and negative (down) spin densities in Ph1- n and

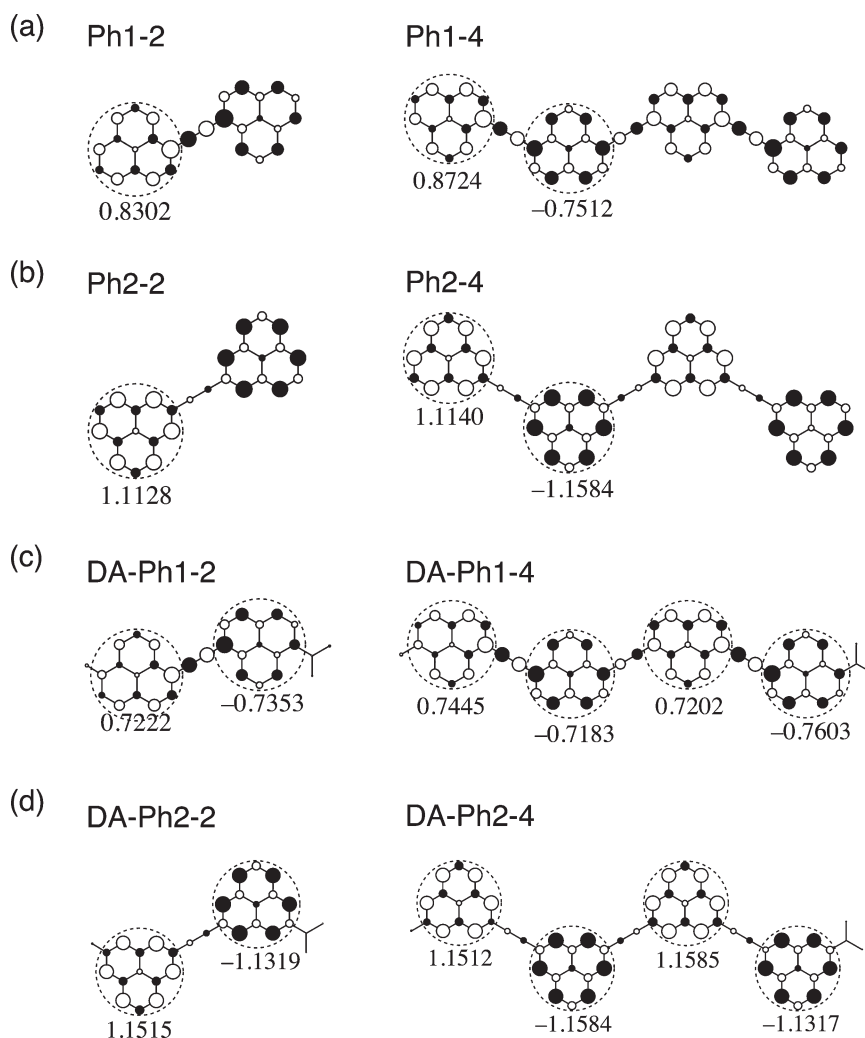


Figure 2. Mulliken spin density distributions (positive: white circle, negative: black circle) for Ph1- n ($n = 2, 4$) (a), Ph1- n ($n = 2, 4$) (b), Ph2- n ($n = 2, 4$) (c), DA-Ph1- n ($n = 2, 4$) (d), and DA-Ph2- n ($n = 2, 4$) (e) calculated using the LC-UBLYP/6-31G* method and the sums of Mulliken spin densities inside the dashed circles.

Ph2- n are alternately distributed on the carbon atoms following the Ovchinnikov's rule,^[64] resulting in an alternation at the level of the phenalenyl rings (see also the sum of the Mulliken spin densities within the dashed circles shown in Fig. 2). The amplitudes of the sum of spin densities are larger in Ph2- n than in Ph1- n , which is consistent with the pure diradical and tetraradical features in Ph2- n , in contrast to the intermediate ones in Ph1- n . Then, the weaker linker-bond interaction in Ph2- n than in Ph1- n is characterized by smaller spin density amplitudes in the linker bonds, that is, the spin density amplitudes on the carbon-carbon bonds in the acetylene linkers: 0.7230 (Ph1-2) vs. 0.2764 (Ph2-2) and [0.6753 (end), 0.5745 (center)] (Ph1-4) vs. [0.2908 (end), 0.2881 (center)] (Ph2-4).

γ of Py-2, Ph1-2, and Ph2-2 are in the 1:12:0.75 ratio. The significant enhancement of γ in Ph1-2 (intermediate diradical) as compared to that in Py-2 (closed shell) and Ph2-2 (pure diradical) is in agreement with the diradical character dependence of γ .^[64] This enhancement is amplified when $n = 4$ with $\gamma(\text{Py-4})/\gamma(\text{Ph1-4})/\gamma(\text{Ph2-4}) = 1:29:0.79$. In other words, γ exhibits a more striking

size dependence for Ph1- n than for Py- n and Ph2- n : $\gamma(4)/\gamma(2) = 4.9$ (Py- n), 12 (Ph1- n), and 5.2 (Ph2- n). The much smaller γ and size dependence for Py- n and Ph2- n are also understood by the negligible π -electron delocalization over the pyrene/phenalenyl rings and the acetylene linkers, which accompany a negligible alternation of the linker-bond lengths (see the previous section). Finally, the comparison of γ for Py- n and Ph1- n with those for Pyn and Phn in Ref. [43], which have similar linked forms, provides somewhat different ratios of γ , that is, $\gamma(\text{Py-2})/\gamma(\text{Ph1-2})/\gamma(\text{Py-4})/\gamma(\text{Ph1-4}) = 1:12:4.9:143$ vs. $\gamma(\text{Py2})/\gamma(\text{Ph2})/\gamma(\text{Py4})/\gamma(\text{Ph4}) = 1:4.2:3.8:44$, though the diradical characters are very similar (see Table 1). It is here noted that the γ expression of a two-site system is given as a function of the diradical character y , a direct exchange integral (K), the difference between the onsite and intersite Coulomb integrals (U), and the effective diradical distance (R): $\gamma = f(y, r_k)R^4/U^3$, where $r_k \equiv 2K/U$.^[6] Usually, r_k is close to zero, and $f(y, 0)$ is maximum in the intermediate y region, which is the origin of the γ enhancement for singlet diradical systems. γ is thus also strongly affected by R : the longer π -conjugated diradical length, the larger the γ value, though this is not the unique tuning parameter. In fact, the γ amplitudes for Pyn and Phn are smaller than those of Py- n and Ph1- n , respectively. This originates from the smaller conjugation length of pyrene/phenalenyl rings in Pyn and Phn than in Py- n and Ph1- n , that is, one benzene ring for Pyn and Phn, whereas two benzene rings for Py- n and Ph1- n in the z direction.

Figure 3 shows that the γ density distributions are dominated by the π -electron contributions. Then, for Ph1- n , extended positive and negative γ densities are primarily distributed on the phenalenyl rings are well separated on the left- and right-hand sides, leading to large positive contributions to γ , whereas Py- n and Ph2- n exhibit much smaller γ density amplitudes, though the positive and negative γ density distributions are also separated on both sides. The extension and left-right separation of the γ density distributions are characteristics of large field-induced third-order polarization, substantiating the link between the diradical character and the enhancement of γ .

DA-substitution effects on the γ of superpolyenes

When substituting the systems by donor (NH_2)/acceptor (NO_2) groups, the DA-Py- n systems remain closed shell, and the DA-Ph2- n systems keep their diradical and tetraradical nature, whereas the open-shell character of the Ph1-based systems

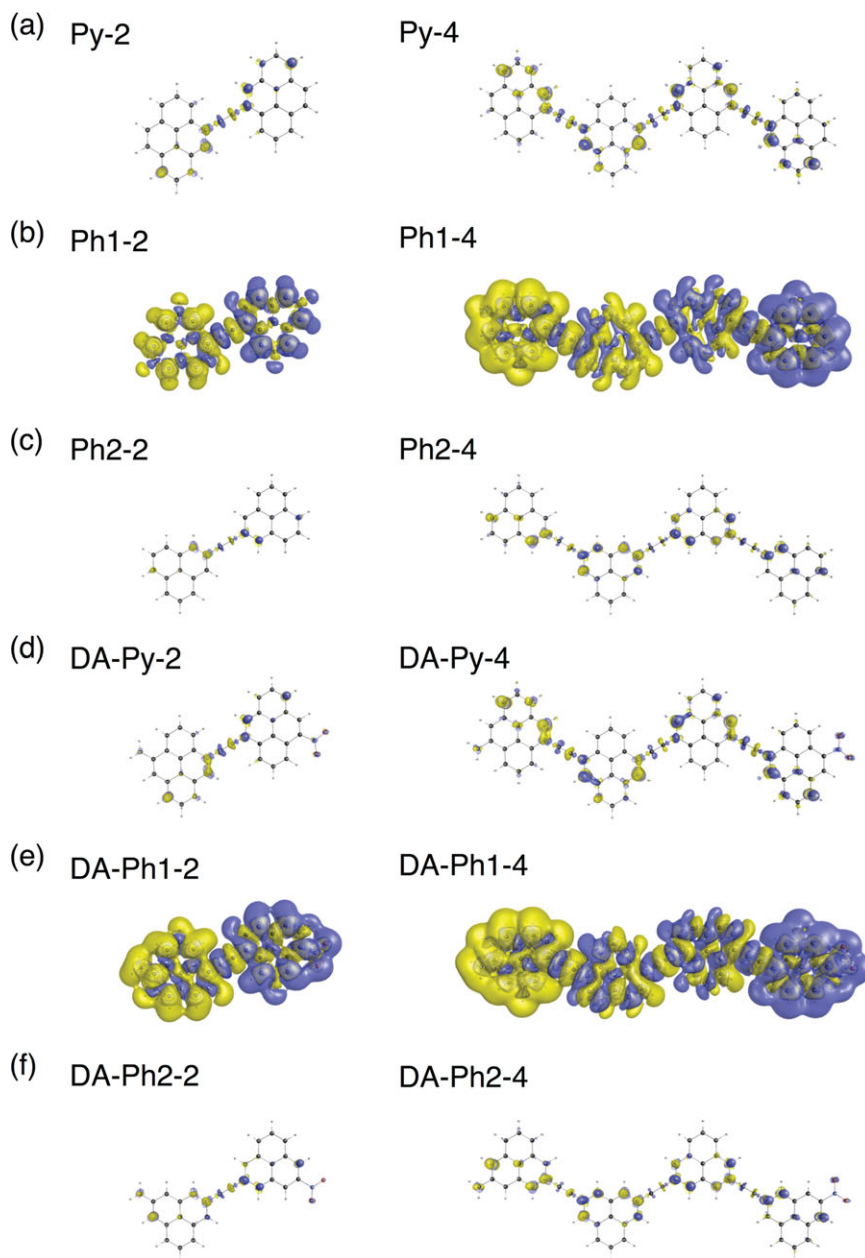


Figure 3. γ_{zzzz} density distributions of Py- n ($n = 2, 4$) (a), Ph1- n ($n = 2, 4$) (b), Ph2- n ($n = 2, 4$) (c), DA-Py- n ($n = 2, 4$) (d), DA-Ph1- n ($n = 2, 4$) (e), and DA-Ph2- n ($n = 2, 4$) (f) calculated using the LC-(U)BLYP/6-31G* method. The yellow and blue surfaces represent positive and negative densities, respectively, with isosurfaces of ± 500 a.u. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreases. Indeed, $y_0 = 0.570$ (Ph1-2) reduces to 0.541 (DA-Ph1-2), and the reduction of $(y_0, y_1) = (0.755, 0.543)$ (Ph1-4) to $(0.661, 0.499)$ (DA-Ph1-4) is larger (Table 1). These features are caused by the relative increase in the ionic characters of the ground state of open-shell singlets with intermediate diradical characters, as modeled by the effect of an external electric field within the two-site valence configuration interaction (VCI) scheme.^[16,17] These variations in diradical characters are represented in Figure 2 where the decrease in the diradical character in DA-Ph1- n corresponds to a spin polarization attenuation, that is, the sum of the Mulliken spin densities in each phenyl

ring becomes smaller than those of the Ph1- n systems, though the antiferromagnetic alignment is kept. On the other hand, for DA-Ph2- n , we observe only a slight change in spin densities on the both-end phenalenyl rings but a much smaller spin density amplitudes in the linker bonds than in DA-Ph1- n . These features are predicted to originate from the weaker linker-bond interaction in DA-Ph2- n than in DA-Ph1- n .

Like for the nonsubstituted compounds, the γ values of DA-Ph1- n are remarkably enhanced as compared to those of DA-Py- n and DA-Ph2- n : $\gamma(\text{DA-Py-}n) : \gamma(\text{DA-Ph1-}n) : \gamma(\text{DA-Ph2-}n) = 1 : 34 : 0.88$ ($n = 2$) and $1 : 44 : 0.81$ ($n = 4$). As a consequence, the enhancement of γ by DA substitution is more significant in the intermediate open-shell character region (Ph1- n) than in the closed-shell (Py- n) and pure open-shell (Ph2- n) regions (see the previous section). This substantiates the VCI analysis^[16,17] where strong field-induced γ enhancements appear in open-shell systems with asymmetric charge distributions and are dominated by type I virtual excitation processes due to the decrease in the first excitation energy and the raise of large dipole moment differences.^[62,65,66]

To clarify the spatial electronic contributions to γ between DA-substituted and nonsubstituted PAHs, we examine their γ density distributions, which are also dominated by π -electron contributions (Fig. 3). DA-Ph1- n show more extended positive and negative γ densities, primarily distributed on the both-end phenalenyl rings substituted by donor (NO_2) and acceptor (NH_2) groups, together with clear left-right separations, leading to larger positive contributions to γ than in their nonsubstituted analogs (Ph1- n). On the other hand, DA-Py- n and DA-Ph2- n exhibit much smaller γ density amplitudes, with the D-A effects limited to the both-end phenalenyl ring

regions, leading to the much smaller enhancements than in DA-Ph1- n . Such a remarkable enhancement of γ and their density distributions in DA-Ph1- n as compared to DA-Py- n and DA-Ph2- n are consistent with the gigantic field-induced γ enhancement described for two-site diradical models with intermediate diradical characters at a zero field.^[17]

Summary

In this study, we have investigated the relationship between the diradical characters and the longitudinal second

hyperpolarizabilities γ of superpolyene systems composed of acetylene-linked phenalenyl/pyrene rings as well as their variations upon substitutions by DA groups. The phenalenyl-based superpolyenes (Ph1-*n*) having intermediate diradical characters exhibit larger γ values than their analogs built from closed-shell pyrene units (Ph2-*n*) and the pure open-shell superpolyenes (Py-*n*). The size dependence of γ is also found to be more significant in Ph1-*n* than in the other systems. These results are in agreement with our predictions on two-site and *N*-site hydrogen chain systems^[67] as well as with those on dipyrrene/diphenalenyl compounds.^[43] In addition, the introduction of DA groups on both-end rings remarkably enhances the γ values in the intermediate open-shell systems (DA-Ph1-*n*) as compared to closed-shell (DA-Py-*n*) and pure open-shell (DA-Ph2-*n*) systems. These results are also consistent with the gigantic field-induced effects on γ in systems with intermediate diradical characters.^[16,17] Although these superpolyenes have not been synthesized yet, this study illustrates the interplay between tuning the diradical characters and exalting the second hyperpolarizabilities as well as their size dependencies while it challenges their synthesis.

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Keywords: open shell · diradical character · second hyperpolarizability · phenalenyl · density functional theory

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