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Masayoshi Nakano [a],[*], Suguru Ohta [a], Kazuya Tokushima [a], Ryohei Kishi [a],
Takashi Kubo [b], Kenji Kamada [c], Koji Ohta [c], Benoît Champagne [d], Edith Botek [d],
Hideaki Takahashi [a]

[a] *Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[b] *Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*
[c] *Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan*
[d] *Laboratoire de Chimie Théorique Appliquée, Facult és Universitaires Notre-Dame de la Paix (FUNDP), Rue de Bruxelles, 61, B-5000 Namur, Belgium*

Abstract

Using hybrid density functional theory methods, the static first (β) and second (γ) hyperpolarizabilities of a donor–acceptor disubstituted singlet diradical system built from phenalenyl radicals linked by an acetylene π-conjugated bridge, DA-BPLE, is investigated and compared to an analogous closed-shell system, DA-BPRY, built from pyrene rings. DA-BPLE presents an intermediate diradical character and exhibits β and γ values about 14 and 7 times larger than those of DA-BPRY having a similar π-conjugation length, respectively. These results suggest the applicability of the structure-property relation in γ of symmetric diradical systems to β and γ of asymmetric diradical systems.
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1. Introduction

Recently, a new strategy of enhancing second hyperpolarizability (γ), which is the microscopic origin of the third-order non-linear optical (NLO) property, has been proposed for symmetric singlet diradical systems with intermediate diradical character [1–8]. The validity of this strategy as well as the reliability and applicability of calculation methods has been computationally confirmed using successive models and real systems: (i) the model of H_2 molecule under dissociation [7], the *p*-quinodimethane (PQM) model [1], the model of twisted ethylene [1], π-conjugated molecules involving imidazole and triazole rings [6] and diphenalenyl radical molecules [4,5,8]. On the basis of these theoretical/computational predictions, Kamada et al.

have recently measured the two-photon absorption (TPA) property (described by the imaginary part of γ) of a singlet diradical hydrocarbon involving diphenalenyl radicals, IDPL and NDPL, synthesized by Kubo et al. [9,10], and have found that the TPA cross section of NDPL records over 8000 GM at 1055 nm, which is the largest value reported so far for pure hydrocarbons [11].

On the other hand, it is well-known that the introduction of donor–acceptor substituents causes the enhancement of γ as well as the emergence of β – the microscopic origin of the second-order NLO property – because it is associated with induced asymmetric charge distribution [12–21]. It has also been predicted that twisted π-electron NLO chromophores, which were predicted to have tunable NLO properties through dihedral twist around a conjugated angle [22,23], bear ground-state diradical characters [24]. These results suggest the existence of unexplored field of asymmetric diradical NLO systems. In particular, for asymmetric systems, remarkable changes are expected not

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[*] Corresponding author. Fax: +81 668506268.
    E-mail address: mnaka@cheng.es.osaka-u.ac.jp (M. Nakano).

only for γ but also for β. In this study, therefore, we investigate the effect of introducing donor–acceptor substituents into diradical and nearly closed-shell systems on their static β and γ using the hybrid density functional theory (DFT) method. As diradical and nearly closed-shell systems, we consider, respectively, the singlet diphenalenyl radical molecule involving an acetylene π-conjugated bridge, i.e., 1,2-bis(phenalen-1-ylidene)ethene (BPLE) [25,26], and bis(pyren-4-yl)ethyne (BPRY) involving pyrene moiety instead of phenalenyl radical moiety. The effects of introducing donor (–OH) and acceptor (–CN) substituents into these molecules on their β and γ values are examined in relation to the diradical characters. From these results, we clarify the diradical character dependence of β and γ for donor–acceptor disubstituted acetylene-bridged diphenalenyl radical systems, and discuss a novel molecular design scheme of second- and third-order NLO systems based on diradical systems with asymmetric charge distribution.

2. Molecular geometries and calculation methods

Fig. 1 shows the schematic structures and resonance structures of a diradical molecule, BPLE (**1**), and a nearly closed-shell hydrocarbon, BPRY (**2**) as well as donor (–OH) – acceptor (–CN) disubstituted BPLE and BPRY, i.e., DA-BPLE (**3**) and DA-BPRY (**4**), in the singlet ground-states. In order to induce asymmetric charge distributions, the positions of the substituents on the phenalenyl rings correspond to positions with significant HOMO distributions in the non-substituted rings. In their optimized structures, all systems are planar, while the non-substituted ones have C_{2h} symmetry. Although the molecular geometries are optimized using the spin-unrestricted (U) B3LYP/6-31G** method, the results of **2** and **4** coincide with those obtained using the spin-restricted (R) B3LYP-method. The alternation between the triple and single bond-lengths in the central acetylene bridge [$\Delta r \equiv \{(r_1 - r_2) + (r_3 - r_2)\}/2$] for **1** ($\Delta r = 0.144$ Å) is smaller than that of **2** ($\Delta r = 0.205$ Å), demonstrating a better conjugation between the rings in compound **1**. These molecular systems are predicted to have contributions of three resonance forms among closed-shell (**a**), open-shell (**b**) and zwitterionic (**c**) structures as shown in Fig. 1. The bond-length differences (Δr) suggest that **1** exhibits an intermediate diradical character between closed-shell **1a** and open-shell (diradical) **1b**, while the zwitterionic **1c** structure is unstable. This is further supported by the Mulliken spin populations, which attain $\pm 0.82|e|$ on each phenalenyl ring. On the other hand, **2** has a more significant contribution from closed-shell structure **2a** than of open-shell (diradical) **2b** and zwitterionic **2c** structures. The introduction of donor (–OH) and acceptor (–CN) substituents does not significantly modify the geometrical differences: $\Delta r = 0.129$ Å (**3**) and $\Delta r = 0.205$ (**4**), although the difference is larger between **1** and **3** than **2** and **4**. Compound **3** displays an intermediate structure between non-charge-transfer (non-CT) (**3a** and **3b**) and CT (**3c**), as well as between closed-

shell (**3a** and **3c**) and open-shell (diradical) (**3b**). Mulliken charge population analysis shows that, with respect to compound **1**, there is a transfer of 0.05 electron from the OH-substituted phenalenyl to the cyano-substituted phenalenyl while the excess electronic charge on the bridge remains close to 0.12 electron. The Mulliken spin populations remain localized on the substituted phenalenyl rings and attain $\pm 0.78|e|$. On the other hand, the geometrical parameters and closed-shell nature of **4** are consistent with a dominant contribution of **4a** (non-CT, closed-shell), because the generation of radical sites in pyrene ring is unstable (see **4c**). This is substantiated by the larger Δr value (0.205 Å), the smaller CT ($0.02|e|$) between the phenalenyl rings with respect to compound **2**, and the smaller magnitude of the x component of ground-state dipole moment ($\mu_x = -0.4772$ a.u. with respect to $= -1.1815$ a.u. for **3**) (see Table 1).

The diradical character is obtained from the spin-unrestricted Hartree–Fock (UHF) calculation. The diradical character y_i related to the HOMO $- i$ and LUMO $+ i$ is defined by the weight of the doubly-excited configuration in the multi-configurational (MC)-SCF theory and is formally expressed in the case of the spin-projected UHF (PUHF) theory as [27,28]

$$y_i = 1 - \frac{2T_i}{1 + T_i^2}, \tag{1}$$

where T_i is the orbital overlap between the corresponding orbital pairs [27,28] ($\chi_{\text{HOMO}-i}$ and $\eta_{\text{HOMO}-i}$) and can also be represented by using the occupation numbers (n_i) of UHF natural orbitals (UNOs):

$$T_i = \frac{n_{\text{HOMO}-i} - n_{\text{LUMO}+i}}{2}. \tag{2}$$

The PUHF diradical character, y_i, takes the value between 0 and 1, which represents the closed-shell and pure diradical states, respectively. The present calculation scheme using the UNOs is the simplest but it can well reproduce the diradical characters calculated by other methods such as the ab initio configuration interaction (CI) method [28,29]. Table 1 gives the diradical characters y calculated from Eqs. (1) and (2) using the occupation numbers of HOMO and LUMO of UNOs (using 6-31G**) for **1–4**. As seen from the diradical characters of **1** ($y = 0.653$) and **2** ($y = 0.192$)[1], **1** possesses an intermediate diradical character, whereas **2** a significant closed-shell character. The introduction of donor (–OH) – acceptor (–CN) substituents into these molecules, leading to **3** ($y = 0.626$) and **4** ($y = 0.199$), hardly changes the diradical characters of non-substituted molecules, consistently with the previous description of the geometry and charge distributions.

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[1] The closed-shell solution of **2** ($y = 0$) obtained by the UHF/6-31G** reported in our previous Letter [5] was later found to possess a triplet instability, so that the diradical character (obtained from the stable open-shell solution) is rectified as $y = 0.192$.
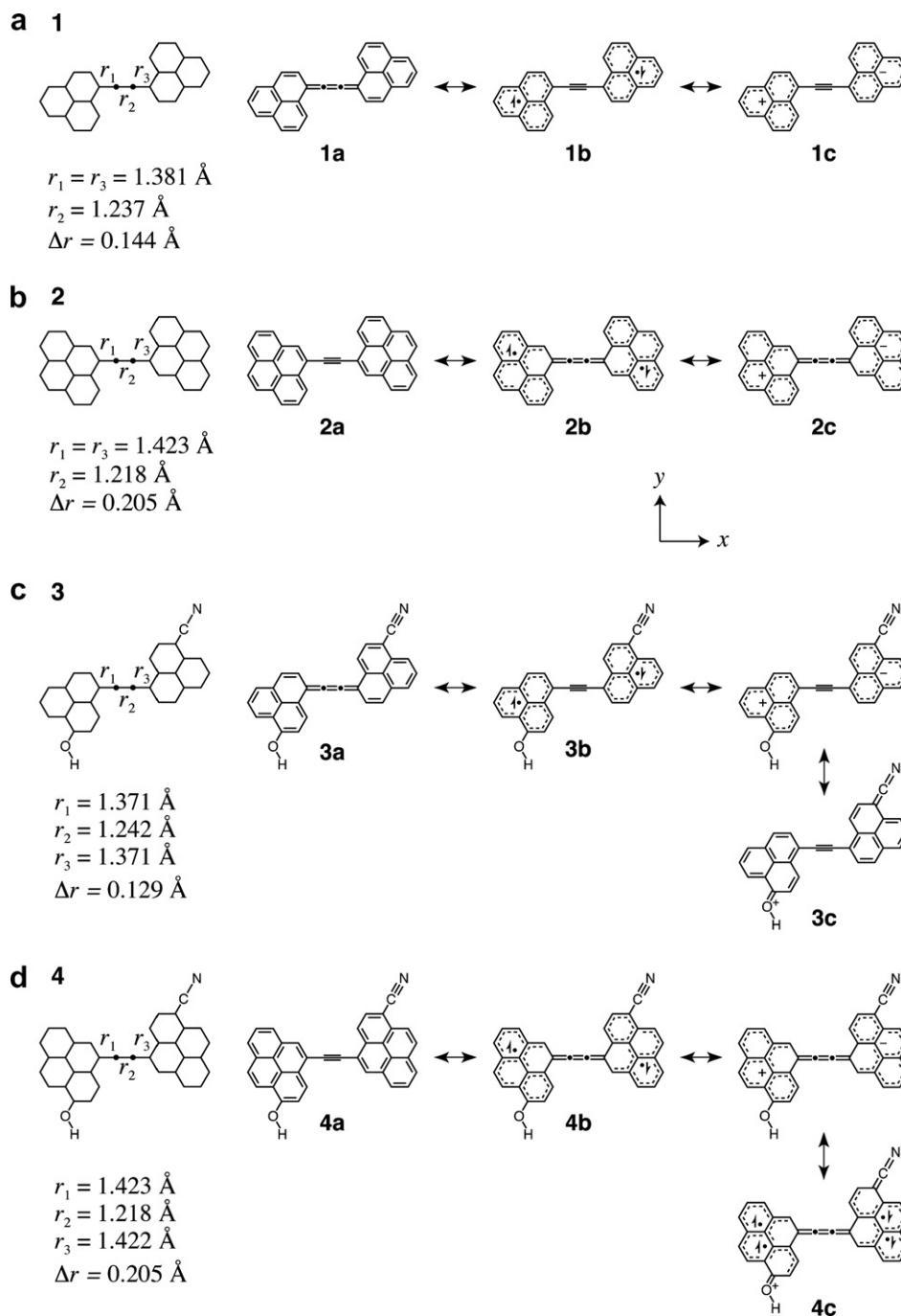
Fig. 1. Molecular geometries, main resonance forms [closed-shell (**a**), open-shell (diradical) (**b**) and zwitterionic (**c**)] of the singlet ground-states of BPLE (**1**), BPRY (**2**), DA-BPLE (**3**) and DA-BPRY (**4**). Coordinate axes, bond-lengths of central acetylene bridges and the difference $\Delta r[\equiv \{(r_1 - r_2) + (r_3 - r_2)\}/2]$ calculated using the B3LYP approach and the 6-31G** basis set are also shown.

We then employed the spin-unrestricted (U) BHandH-LYP method [30] for **1** and **3** and the spin-restricted (R) BHandHLYP method for **2** and **4** for calculating the longitudinal β (β_{xxx}) and γ (γ_{xxxx}) values, in agreement with the study on PQM showing that the UBHandHLYP and RBHandHLYP methods can reproduce highly electron correlated γ values, e.g., UCCSD(T) γ values, for the intermediate diradical molecules and for the closed-shell or diradical molecules with small diradical characters, respec-

tively [1]. In fact, for **2** and **4**, the UBHandHLYP method converges to the RBHandHLYP solutions, which indicates that these molecules are regarded as closed-shell systems at the BHandHLYP level of approximation. Although it is well-known that the use of extended basis sets are necessary for obtaining quantitative β and γ values for small π-conjugated systems [31], we use the standard basis set, 6-31G*, which was shown to be sufficient for, at least, qualitative comparison of the longitudinal components of γ for

Table 1
Diradical character (y), dipole moment (μ_x)*, first (β_{xxx})* and second (γ_{xxxx})* hyperpolarizabilities of BPLE (**1**), BPRY (**2**), DA-BPLE (**3**) and DA-BPRY (**4**) shown in Fig. 1

System	y	μ (a.u.)	β ($\times 10$ a.u.)	γ ($\times 10^4$ a.u.)
1	0.653	0	0	157
2	0.192	0	0	36
3	0.626	−1.1815	−1340	265
4	0.199	−0.4772	−98	39

*1.0 a.u. of $\mu = 8.4784 \times 10^{-30}$ $C_m = 2.5418 \times 10^{-18}$ esu, $\beta = 3.2063 \times 10^{-53}$ $C^3m^3J^{-2} = 8.6391 \times 10^{-33}$ esu and 1.0 a.u. of $\gamma = 6.2353 \times 10^{-65}$ $C^4m^4J^{-3} = 5.0367 \times 10^{-40}$ esu. The calculations of diradical characters are performed using the occupation numbers of UNOs (using 6-31G** basis set) and those of μ, β and γ are done using the UBHandHLYP method for **1** and **3** and RBHandHLYP method for **2** and **4** with the 6-31G* basis set.

relatively large-size hydrocarbons involving phenalenyl radicals [4,5]. We confine our attention to the dominant longitudinal components of static β (β_{xxx}) and γ (γ_{xxxx}) (see Fig. 1) using the finite field (FF) approach [32], which consist of the third- and fourth-order energy (E) derivatives with respect to the applied external electric field. The power series expansion convention (usually called B convention) is chosen for defining β and γ. We adopt the following numerical differentiation procedure [33]:

$$\beta = \{-E(3F) + 8E(2F) - 13E(F) + 13E(-F) \\ - 8E(-2F) + E(-3F)\}/4(F)^3 \quad (3)$$

and

$$\gamma = \{E(3F) - 12E(2F) + 39E(F) - 56E(0) \\ + 39E(-F) - 12E(-2F) + E(-3F)\}/36(F)^4. \quad (4)$$

Here, $E(F)$ corresponds to the total energy in the presence of the field F applied in the longitudinal direction. We employ the magnitude of F ranging from 0.0005 to 0.0020 a.u. in order to obtain numerically stable β and γ values within an error of 1%. All calculations are performed using the GAUSSIAN 03 program package [30].

3. First and second hyperpolarizability density analyses

We employ the first (β) and second (γ) hyperpolarizability density analyses [33] in order to characterize the spatial contributions of electrons to β and γ. The contributions obtained from a pair of positive and negative β and γ densities (see Eqs. (5) and (6)) provide a description of local contributions of electrons to the total β and γ, respectively, as given by

$$\beta = -\frac{1}{2!}\int r\rho^{(2)}(r)d^3r \quad \text{and} \quad \gamma = -\frac{1}{3!}\int r\rho^{(3)}(r)d^3r, \quad (5)$$

where

$$\rho^{(2)}(\boldsymbol{r}) = \frac{\partial^2\rho(\boldsymbol{r})}{\partial F^2}\bigg|_{F=0} \quad \text{and} \quad \rho^{(3)}(\boldsymbol{r}) = \frac{\partial^3\rho(\boldsymbol{r})}{\partial F^3}\bigg|_{F=0}. \quad (6)$$

It is noted that the positive and negative values of $\beta(\gamma)$ densities multiplied by $F^2(F^3)$ correspond respectively to the field-induced increase and decrease in the second (third)-order charge density (proportional to $F^2(F^3)$), which induce the second (third)-order dipole moment [second (third)-order polarization] in the direction from positive to negative $\beta(\gamma)$ densities. Therefore, the $\beta(\gamma)$ density map represents the relative phase and magnitude of change in the second (third)-order charge densities between two spatial points with positive and negative values. The $\beta(\gamma)$ densities are calculated for a grid of points using a numerical second (third)-order differentiation of the electron densities calculated by GAUSSIAN 03. The origin is chosen to be the molecular centre of mass, XY defines the molecular plane, and the central acetylene bridge of the molecule is taken to be the X-axis. The box dimensions ($-12 \leqslant x \leqslant 12$ Å, $-10 \leqslant y \leqslant 10$ Å and $-5 \leqslant z \leqslant 5$ Å) ensure that the $\beta(\gamma)$ values obtained by integration are within 1% of the FF results. For instance, for a pair of localized $\beta(\gamma)$ densities with positive and negative values the sign of the contribution to $\beta(\gamma)$ is positive when the direction from positive to negative $\beta(\gamma)$ density coincides with the positive direction of the coordinate system. The sign becomes negative in the opposite case. The magnitude of the contribution associated with this pair of $\beta(\gamma)$ densities is proportional to the distance between them.

4. Results and discussion

The $\beta_{xxx}(\beta)$ and $\gamma_{xxxx}(\gamma)$ values of **1**–**4** calculated by the BHandHLYP/6-31G* method are given in Table 1. The γ value of **1** ($y = 0.653$ and $\gamma = 157 \times 10^4$ a.u.) is about four times as large as that of **2** ($y = 0.192$ and $\gamma = 36 \times 10^4$ a.u.), which is in agreement with our prediction that the system with intermediate diradical character exhibits much larger γ value than that with small diradical character [1,5]. Since the solutions for **1** and **3** (in contrast to **2** and **4**) are symmetry-broken (spin-polarized), their α and β spin density distributions were analyzed at the UBHandHLYP/6-31G* level (Fig. 2). For these singlets, they describe the correlation between the α and β spins, though such distributions cannot be measured. In **1**, the α and β spin densities alternate on the right- and left-hand side phenalenyl rings, respectively, while spin polarization appears in the bridge region. The introduction of donor (–OH) and acceptor (–CN) substituents into phenalenyl rings of **1** hardly changes the spin density distributions as well as the diradical character. These spin density distributions substantiate the intermediate diradical character of **1** and **3**. The magnitude of β values of **3** ($y = 0.626$ and $\beta = -1340 \times 10$ a.u.) is about 14 times as large as that of **4** ($y = 0.199$ and $\beta = -98 \times 10$ a.u.), the feature of which suggests that our structure-property relation of diradical molecules is also applicable to β values. It is further found that the γ value for **3** ($y = 0.626$ and $\gamma = 265 \times 10^4$ a.u.) is about 7 times enhanced compared to that for **4** ($y = 0.199$ and $\gamma = 39 \times 10^4$ a.u.), and the increase rate, γ
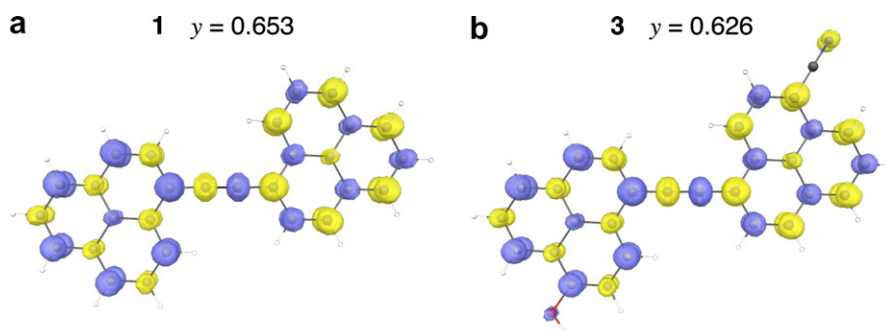
Fig. 2. Spin density distributions of BPLE (**1**) and DA-BPLE (**3**) calculated at the UBHandHLYP/6-31G* level as well as diradical characters y. The yellow and blue surfaces represent α and β spin densities with the iso-surfaces with 0.01 a.u. and -0.01 a.u., respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(DA-substituted)/γ (non-substituted), by the introduction of donor (–OH) and acceptor (–CN) substituents are 1.7 for structure **1** and 1.08 for structure **2**. From these results, donor–acceptor disubstituted π-conjugated systems with intermediate diradical character are expected to exhibit fur-

ther enhanced γ values as compared to donor–acceptor disubstituted and non-substituted systems with smaller diradical characters.

It is interesting to note that the γ values for compounds **1** and **3** are larger than those of the best conjugated oligo-
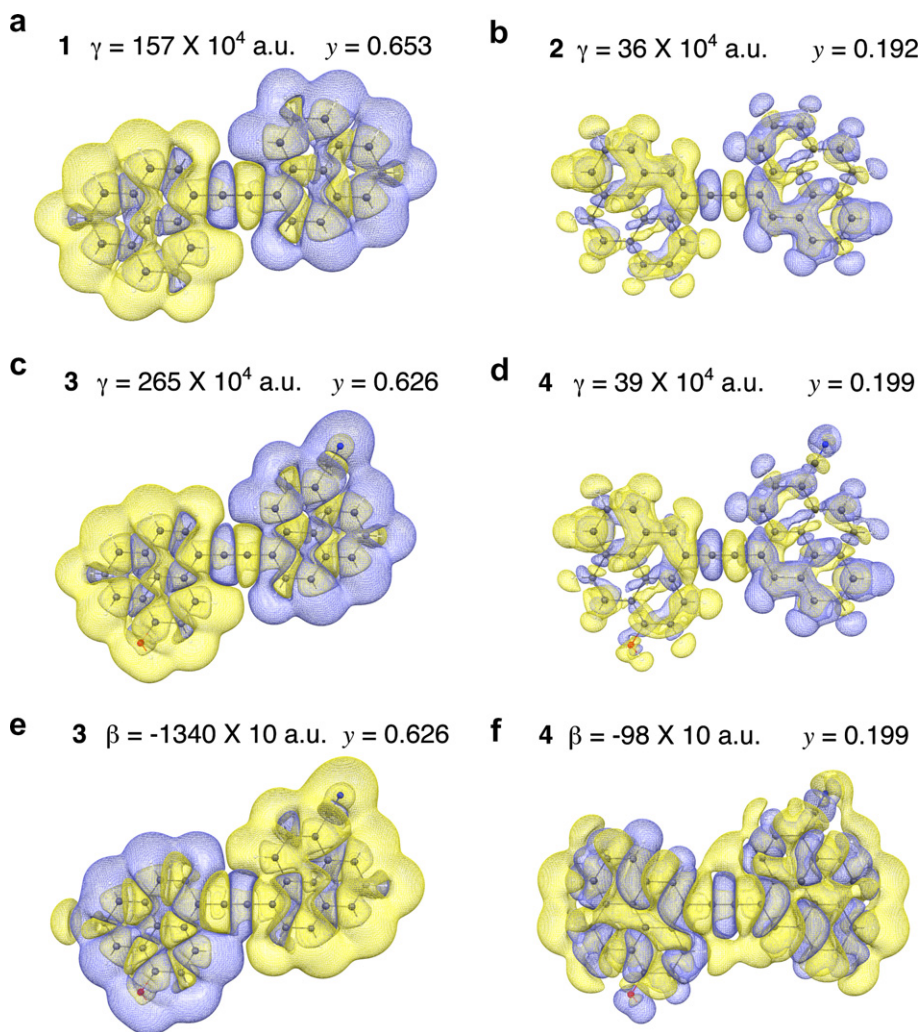

Fig. 3. γ density distributions for total electron contributions in the singlet ground-states of BPLE (**1**), BPRY (**2**), DA-BPLE (**3**) and DA-BPRY (**4**), and β density distributions for those of DA-BPLE (**3**) and DA-BPRY (**4**). γ values and diradical characters y are also shown. The yellow and blue meshes represent positive and negative β (γ) densities with iso-surfaces with ± 0.1 (± 100) a.u., respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

mers of similar size. For instance, γ of the trimer of poly-butatriene – which is made of 12 C atoms – attains 700×10^3 a.u. as determined at the MP2/6-31G* level of approximation [34]. On the other hand, the corresponding β value of compound **3** is not necessarily larger than these of typical D/A π-conjugated systems. For instance, using MP2/6-31G calculations on NH_2–$(CH=CH)_6$–NO_2 β attains 313×10^2 a.u. [35] with respect to 134×10^2 a.u. for compound **3**, demonstrating that the nature and position of the D/A in BPLE could still be optimized.

The β and γ density distributions for these molecules are shown in Fig. 3. For all systems, the main contributions stem from the π-electrons, while the σ-electrons exhibit a γ contribution of opposite sign but much smaller amplitude. For **1** and **3**, the dominant and positive contributions to γ come from the extended positive and negative γ densities well-separately distributed on the left and right phenalenyl ring regions, respectively, though small opposite (negative) contributions appear in the central C–C regions. The small γ values of **2** and **4** are represented by significantly reduced γ densities on both end pyrene rings. From the comparison of γ densities between donor–acceptor disubstituted and non-substituted systems, the introduction of donor and acceptor substituents (**3** and **4**) enhances little the amplitudes of γ densities for **1** and **2**, respectively, except for the additional distributions on donor and acceptor substituents. The β density distribution of **3** is shown to be similar to its γ density distribution, whereas for **4**, the positive and negative contributions to β significantly cancel each other so that the β amplitude is small. In both cases, the first hyperpolarizability and dipole moment are parallel. These features of β and γ density distributions substantiate the relative magnitudes and signs of β and γ values of these systems.

5. Concluding remarks

We have investigated the β and γ values of the singlet donor (–OH) – acceptor (–CN) disubstituted diradical systems built from phenalenyl radical rings linked by an acetylene π-conjugated bridge, DA-BPLE (**3**), and compared these to an analogous closed-shell systems made of pyrene units, DA-BPRY (**4**) as well as to corresponding reference systems, BPLE (**1**) and BPRY (**2**). The β and γ values of DA-BPLE (**3**) are about 14 and 7 times larger than those of DA-BPRY (**4**), respectively. The main contribution to this significantly enhanced γ arises from the phenalenyl radical moieties at both ends. The introduction of donor and acceptor substituents is also found to enhance the γ values for BPLE (**1**) and BPRY (**2**) by a factor of 1.7 and 1.06, respectively. The present study suggests the applicability of the γ structure-property relationships of symmetric diradical systems to the β and γ of asymmetric donor–acceptor disubstituted systems, though appropriate substituents with specific donor and acceptor strengths have to be selected to tune the diradical character and maximize the NLO responses. The extent to which the diradical charac-

ter will change with the substituent D/A strengths remains also to be investigated as well as the calculation of the mean hyperpolarizabilities.

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