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# The Odd Electron Density Is the Guide toward Achieving Organic Molecules with Gigantic Third-Order Nonlinear Optical Responses

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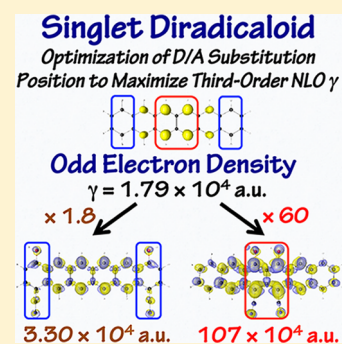
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**S** Supporting Information

**ABSTRACT:** Using density functional theory, the central role of the odd electron density for designing open-shell singlet compounds with enhanced second hyperpolarizabilities [third-order nonlinear optical (NLO) properties at the molecular level] is evidenced. Its amplitude, corresponding to the diradical character, gives the potential of enhancement, whereas its spatial distribution indicates where the donor and acceptor substituents should be placed to further increase this third-order NLO response. This is illustrated by comparing hexacenes, open-shell singlet graphene nanoflakes with intermediate diradical character, with reference closed-shell terylenes. Enhancements up to 2 and 3 orders of magnitude are achieved when the OH/CN and NH<sub>2</sub>/NO<sub>2</sub> substituents are placed in the middle of the zigzag edge region, which corresponds to the largest odd electron density amplitude.

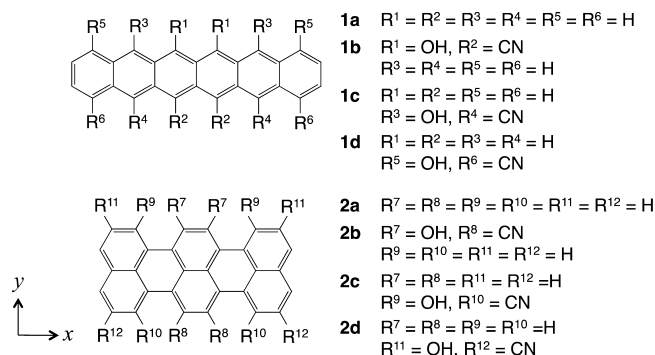
**SECTION:** Plasmonics, Optical Materials, and Hard Matter



The second hyperpolarizability ( $\gamma$ ) is a subtle molecular property that depends on several structural and electronic parameters. Its optimization is, however, of high technological relevance since it will give rise to materials with large third-order nonlinear optical (NLO) responses for applications in holographic imaging, frequency mixing, and telecommunications.<sup>1</sup> So far, to optimize  $\gamma$ , several design guidelines have been deduced from combined experimental and theoretical investigations: (i) increasing the conjugation length,<sup>2–4</sup> (ii) introducing appropriate substituents with specific donor (D) and acceptor (A) strengths,<sup>5,6</sup> (iii) adjusting the shape and dimensionality of the  $\pi$ -electron network,<sup>7,8</sup> and (iv) tuning the charge.<sup>9–12</sup> Still, there remain possibilities to further enhance  $\gamma$ , as suggested by the fundamental limits obtained using the Thomas–Kuhn sum rule.<sup>13,14</sup>

As demonstrated by the substantial  $\gamma$  exaltation, some of these new compounds are open-shell systems, provided they display an intermediate diradical character ( $y$ ).<sup>15–21</sup> The initial proof of this  $y$ – $\gamma$  relationship was derived from purely theoretical arguments,<sup>15,16</sup> but subsequent experimental measurements have confirmed it.<sup>17–21</sup>  $y$ , which is a chemical index of bond strength or of electron localization in the bond,<sup>22–25</sup> governs the excitation energies and the transition moments,<sup>15,26</sup> and is thus a key quantity for designing molecules with large  $\gamma$ <sup>27,28</sup> as well as for describing other intriguing photochemical phenomena, e.g., the feasibility conditions of singlet fission, which boosts the energy conversion efficiency of organic solar cells.<sup>29,30</sup> This has led to the design of molecules with large  $\gamma$  by tuning  $y$  through the modification of the  $\pi$ -conjugation length,<sup>31</sup> of the (anti)aromatic character,<sup>32,33</sup> or of the d–d orbital interactions.<sup>34</sup> However, since  $y$  is a molecular property,

it does not tell a priori where to put the D/A substituents, while there are examples of  $\gamma$  enhancements upon substitutions.<sup>35,36</sup> In this Letter, we show that the odd electron density is the missing link to tune  $y$  through adequately placing D/A substituents. Then, owing to the remarkable electronic properties of graphene,<sup>37,38</sup> this new design approach is illustrated by considering graphene nanoflakes (GNFs), typical open-shell singlet systems (Figure 1). Hexacene (**1a**) as well as its D/A-tetrasubstituted analogues (**1b–d**) were chosen because they present small or intermediate  $y$  values, whereas



**Figure 1.** Structures of hexacenes (**1a–d**) and terylenes (**2a–d**) with/without donor (OH) and acceptor (CN) groups and coordinate axes.

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the corresponding terrylenes (**2a–d**) were selected as reference closed-shell GNF systems.

The open-shell character of a molecule can be described by the spatial distribution of the odd electron densities<sup>39,40</sup>  $D_{\text{LUNO}}^{\text{odd}}(\mathbf{r})$  and  $D_{\text{HONO}}^{\text{odd}}(\mathbf{r})$ , where HONO and LUNO are the highest occupied and the lowest unoccupied natural orbitals, respectively, according to<sup>24</sup>

$$D_y^{\text{odd}}(\mathbf{r}) = D_{\text{HONO}}(\mathbf{r}) + D_{\text{LUNO}}(\mathbf{r}) \quad (1)$$

where each of the contributions is defined as<sup>40</sup>

$$D_k^{\text{odd}}(\mathbf{r}) = \min(2 - n_k, n_k) \phi_k^*(\mathbf{r}) \phi_k(\mathbf{r}) \quad (2)$$

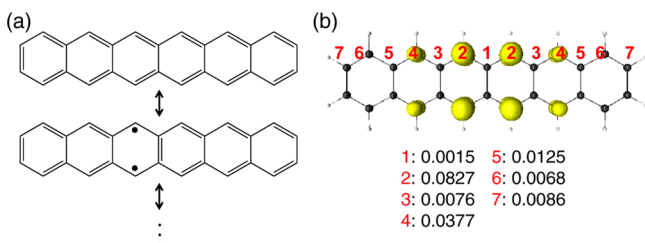
$\min(2 - n_k, n_k)$  can thus be regarded as the probability for the electron of being unpaired in  $\phi_k(\mathbf{r})$ . In the case of  $n_{\text{HONO}} + n_{\text{LUNO}} = 2$ , which is satisfied exactly in single-determinant schemes and approximately in general, the diradical character reads<sup>24</sup>

$$y = \frac{1}{2} \text{Tr}[D_y^{\text{odd}}(\mathbf{r})] \quad (3)$$

highlighting that the spatial distribution of  $y$  is described by the odd electron densities.  $y$  ranges from 0 (closed-shell) to 1 (pure diradical). It is here evaluated as the occupation number ( $n_{\text{LUNO}}$ ) of the LUNO, equal also to  $2 - n_{\text{HONO}}$  [ $n_{\text{HONO}}$ : occupation number of the HONO] within single determinant schemes.

The spin-unrestricted density functional theory (UDFT) method with the B3LYP/6-31G\* functional was employed to optimize the molecular structures. For molecules **1b**, **1c**, and **2a–d**, the UB3LYP/6-31G\* solutions reduce to the spin-restricted ones. Frequency analyses confirmed that the optimized structures are minima. The nonsubstituted systems **1a** and **2a** display perfectly planar structures (on the  $x$ – $y$  plane) with  $D_{2h}$  symmetries. The end-substituted systems (**1d**, **2d**) are almost planar with slight distortions. In contrast, middle(**1b**, **2b**)- and intermediate(**1c**, **2c**)-substituted systems somewhat show out-of-plane structures owing to the steric hindrances between neighboring substituents (see Tables 1S–8S in the Supporting Information).

$y$  and  $\gamma$  were calculated using the long-range corrected spin-unrestricted exchange-correlation functional, LC-UBLYP,<sup>41</sup> with a range separating parameter set to 0.33, combined with the 6-31+G\* basis set. The finite field approach<sup>42</sup> was employed to evaluate the diagonal component of  $\gamma$  perpendicular to the acene growing direction ( $\gamma_{yyyy}$ ), i.e., in the direction joining the radical sites (see Figure 2a). The spatial electronic contributions to  $\gamma$  was probed using the  $\gamma$  density,  $\rho^{(3)}(\mathbf{r})$ ,<sup>10</sup> calculated from the third-order derivative of



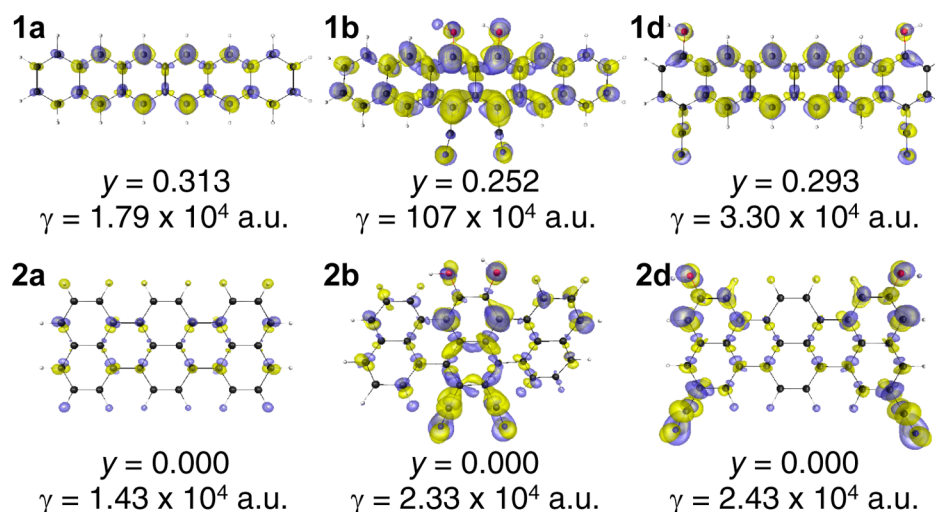
**Figure 2.** Resonance structures (a) and ground-state odd electron density [ $D_y^{\text{odd}}(\mathbf{r})$ , iso-surfaces of 0.002 a.u.] distribution (b) of hexacene calculated using the LC-UBLYP/6-31+G\* method. Mulliken odd electron populations on carbon atom sites 1–7 are also shown.

the electron density with respect to external electric fields. Positive and negative  $\rho^{(3)}(\mathbf{r})$  respectively indicate the field-induced increase and decrease of the electron density in proportion to the third power of the external field, a pair of which along the  $y$ -axis gives a positive contribution to the  $\gamma_{yyyy}$ . It was also worth addressing the spin contamination effects on the  $y$  and  $\gamma$  values since they can lead to incorrect results, e.g., on the singlet–triplet energy gaps,<sup>43</sup> while they depend on the exchange-correlation functionals in the UDFT method.<sup>44,45</sup> Thus, we applied the approximate spin projection scheme,<sup>24,25,45</sup> which can correct the spin contamination, to the present molecules, and confirmed that this method predicts the same  $y$ – $\gamma$  relationship (see section 3 in the Supporting Information). All calculations were performed using the Gaussian 09 program package.<sup>46</sup> More details can be found in the Supporting Information.

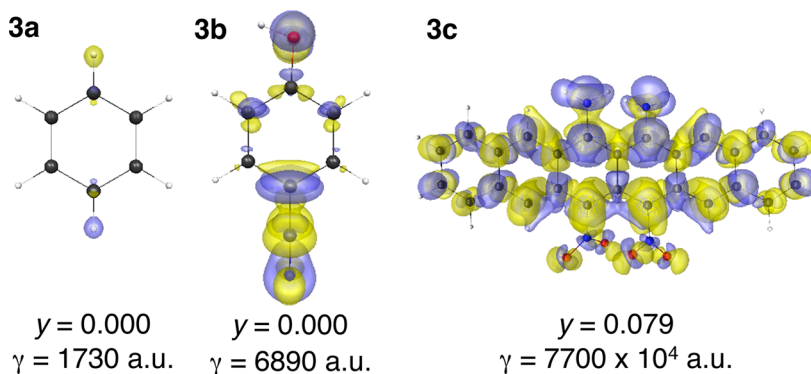
For the nonsubstituted species,  $y$  of molecule **2a** is zero, indicating a closed-shell state, while molecule **1a** exhibits an intermediate  $y$  value (0.313), with an odd electron density mostly distributed in the middle zigzag edge regions (see Figure 2b). Substantiating the  $\gamma$  enhancement caused by intermediate diradical characters,  $\gamma$  of **1a** ( $\gamma = 1.79 \times 10^4$  a.u.) is 1.25 times as large as that of molecule **2a** ( $\gamma = 1.43 \times 10^4$  a.u.), though in molecule **1a** ( $\text{C}_{26}\text{H}_{16}$ ) the number of  $\pi$ -electrons and the  $\pi$ -conjugation length in the  $y$ -direction are smaller than those of molecule **e** ( $\text{C}_{30}\text{H}_{16}$ ).

The substituent effects are assessed by comparing molecules **1b–d** and **2b–d**. Molecule **2b** is a closed-shell system, like **2a**, but molecule **1b** ( $y = 0.252$ ) is an open-shell singlet system with a  $y$  value smaller than in **1a**. Such reduction of  $y$  due to substitutions, generally observed in open-shell singlet molecules,<sup>35</sup> originates from an increase of ionic character of the ground state.  $\gamma$  values of **1b** and **2b** amount to  $107 \times 10^4$  a.u. and  $2.33 \times 10^4$  a.u., respectively, highlighting a remarkable difference of enhancement ratios for the substituted/non-substituted systems, i.e.,  $\gamma(\mathbf{1b})/\gamma(\mathbf{1a}) = 59.8$  versus  $\gamma(\mathbf{2b})/\gamma(\mathbf{2a}) = 1.63$ . This striking effect due to D/A-substitution is attributed to the intermediate diradical character. In order to clarify the impact of the substitution position on  $y$ , intermediate (**1c**)- and end (**1d**)-substituted hexacenes were also examined.  $\gamma$  of **1c** and **1d** attain  $12.5 \times 10^4$  and  $3.30 \times 10^4$  a.u., respectively, corresponding therefore to smaller enhancement ratios [ $\gamma(\mathbf{1c})/\gamma(\mathbf{1a}) = 6.98$  and  $\gamma(\mathbf{1d})/\gamma(\mathbf{1a}) = 1.84$ ] than for **1b**. In sharp contrast, the substituted terrylenes (**2b–d**) present similar  $\gamma$  values to **1d**. Thus, the larger the  $\gamma$  value, the larger the change of  $y$  upon substitution, the smaller the  $y$  value [ $y$  values decrease according to the sequence **1a** (0.313) > **1d** (0.293) > **1c** (0.269) > **1b** (0.252)], and the more central the substitution position. As displayed in Figure 2b, these effects are directly linked to the spatial contributions to the diradical character of **1a**:  $D_y^{\text{odd}}(\mathbf{r})$  exhibits dominant amplitudes in the middle zigzag edge regions, it decreases as going toward the end regions, and has negligible amplitudes in the end regions (see also the Mulliken odd electron populations on sites 1–7 in Figure 2b). The variations of  $y$  upon substitution therefore parallel the odd electron density, explaining therefore the increase of the ionic contribution to  $\gamma$  and its exaltation. Moreover,  $\gamma$  increases nonlinearly as a function of the odd electron density of the substituted position, i.e., the Mulliken odd electron populations are in the 1:5.5:12 ratio for the **1d**:**1c**:**1b** compounds, whereas the corresponding  $\gamma$  are in a 1:3.8:32 ratio.

In order to clarify the spatial electronic contributions to  $\gamma$ , we also investigated the  $\gamma$  density [ $\rho^{(3)}(\mathbf{r})$ ] distributions of the



**Figure 3.**  $\gamma$  density [ $\rho^{(3)}(r)$ ] distributions for hexacenes (**1a**, **1b**, **1d**) and terrylenes (**2a**, **2b**, **2d**) as well as their diradical characters ( $y$ ) and  $\gamma$  values calculated using the LC-UbLYP/6-31+G\* method. The yellow (blue) meshes represent positive (negative)  $\rho^{(3)}(r)$  with iso-surfaces of  $\pm 150$  a.u. for **1a** and **1d**,  $\pm 4000$  a.u. for **1b**, and  $\pm 40$  a.u. for **2a**, **2b** and **2d**.



**Figure 4.**  $\gamma$  density [ $\rho^{(3)}(r)$ ] distributions for benzene (**3a**), 4-hydroxybenzonnitrile (**3b**), and hexacene with two  $\text{NH}_2/\text{NO}_2$  substituent pairs in the middle region (**3c**) as well as their diradical characters ( $y$ ) and  $\gamma$  values calculated using the LC-UbLYP/6-31+G\* method. The yellow (blue) meshes represent positive (negative)  $\rho^{(3)}(r)$  with iso-surfaces of  $\pm 40$  a.u. (**3a** and **3b**) and  $\pm 150000$  a.u. (**3c**).

hexacene and terrylene derivatives (Figure 3 and also Figure 3S in the Supporting Information). For compounds **1a–d**, the primary amplitudes are located in the middle zigzag edge regions, which coincide with the regions with large odd electron densities, whereas for **2b–d**, the largest  $\rho^{(3)}(r)$  amplitudes follow the D/A substituents positions and the C atoms attached to them. This supports the conclusion that the significant  $\gamma$  enhancement in hexacenes relative to terrylenes originates from the open-shell character, associated with the dominant odd electron densities (see sites 2 and 4 in Figure 2b). On the contrary, in terrylenes, the enhancement is only driven by the substituents, as in traditional push–pull compounds.<sup>5,6</sup> The  $\rho^{(3)}(r)$  amplitudes also follow the  $\gamma$  ordering, i.e., **1b** > **1c** > **1d** > **1a** and **2b**  $\sim$  **2c**  $\sim$  **2d** > **2a**. The much larger  $\rho^{(3)}(r)$  amplitudes in the middle of molecule **1b** than at the edges of molecule **1d** also demonstrates that the charge transfer (CT) effects are enhanced in **1b** due to its open-shell character and the largest odd electron density on sites 2 (Figure 2).

In order to substantiate this prediction, using the same approach, we performed a comparison between benzene (**3a**) and 4-hydroxybenzonnitrile (**3b**) (shown in Figure 4), one of the simplest closed-shell D- $\pi$ -A aromatic molecules.  $\gamma$  of benzene and of 4-hydroxybenzonnitrile amount to 1730 and 6890 a.u., respectively. The enhancement between **3a** and **3b** comes from

the CT between the OH and CN groups presenting large negative and positive amplitudes. On the basis of these results, substitution of a closed-shell system by a D(OH)/A(CN) pair accounts for an increase of  $\gamma$  by  $\sim 5200$  a.u. per benzene ring. Therefore, assuming additivity of these effects, for molecule **1d**, the  $\gamma$  enhancement with respect to **1a** is estimated to attain  $\sim 10400$  a.u., which corresponds to  $\sim 70\%$  of the total enhancement, demonstrating CT is the dominant effect. In sharp contrast, the substantial  $\gamma$  enhancement ( $105 \times 10^4$  a.u.) in **1b** relative to **1a** can not be explained by such CT effects in closed-shell D- $\pi$ -A systems.

As a consequence, it is expected that  $\gamma$  will be further enhanced by increasing the D/A strength. So, by substituting hexacene in its middle position by the stronger D( $\text{NH}_2$ )/A( $\text{NO}_2$ ) pair (leading to a slightly twisted system as a result of steric hindrance) (**3c**, Figure 4), the diradical character gets smaller ( $y = 0.079$ ) than in molecule **1b**, while  $\gamma$  is enhanced by a factor of  $\sim 4300$  ( $\sim 72$ ) with respect to **1a** (**1b**). Similar to the case of molecule **1b** (Figure 3), the  $\gamma$  density amplitudes on the zigzag edges are strongly enhanced by the D/A substitutions, which reveals that the dominant contribution to  $\gamma$  is attributed to the CT between the dense odd electron distributions.

In conclusion, using density functional theory, the central role of the odd electron density for designing open-shell singlet

compounds with enhanced second hyperpolarizabilities is evidenced. Its amplitude, corresponding to the diradical character, gives the potential of enhancement, whereas its spatial distribution indicates where the D and A substituents should be placed to further increase this third-order NLO response. Provided strong D/A pairs are adequately placed, i.e., in the region with the largest odd electron density, this allows enhancing the second hyperpolarizabilities by up to 2–3 orders of magnitude. This effect is not observed in closed-shell analogs, neither for open-shell systems substituted at positions with negligible odd electron densities. In addition to pointing out the interest of open-shell systems and particularly of GNFs for NLO, the present study opens a new way to design and control molecules with giant third-order NLO responses by highlighting the guiding role of the odd electron density that points out the best D/A substitution positions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Atomic Cartesian coordinates of the optimized molecular structures and corresponding total energies. Detailed description of the methods for calculation and analysis of the diradical characters and the  $\gamma$  values. Results by using the approximate spin projection scheme with the LC-UBLYP ( $\mu = 0.47$ ) functional.  $\gamma$  density distributions for molecules **1c** and **2c**. Full references for refs 17, 20, 21, 24, 25, 32, 35, and 46. The material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Brédas, J. L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. Third-Order Nonlinear Optical Response in Organic Materials: Theoretical and Experimental Aspects. *Chem. Rev.* **1994**, *94*, 243–278.
- (2) Heflin, J. R.; Wong, K. Y.; Zamani-Khamiri, O.; Garito, A. F. Nonlinear Optical Properties of Linear Chains and Electron-Correlation Effects. *Phys. Rev. B* **1988**, *38*, 1573–1576.
- (3) Toto, J. L.; Toto, T. T.; de Melo, C. P.; Kirtman, B.; Robins, K. Hartree–Fock Static Longitudinal (Hyper)polarizability of Polyene. *J. Chem. Phys.* **1996**, *104*, 8586–8592.

- (4) Tretiak, S.; Chernyak, V.; Mukamel, S. Chemical Bonding and Size Scaling of Nonlinear Polarizabilities of Conjugated Polymers. *Phys. Rev. Lett.* **1996**, *77*, 4656–4659.

- (5) Puccetti, G.; Blanchard-Desce, M.; Ledoux, I.; Lehn, J. M.; Zyss, J. Chain-Length Dependence of the Third-Order Polarizability of Disubstituted Polyenes: Effects of End Groups and Conjugation Length. *J. Phys. Chem.* **1993**, *97*, 9385–9391.

- (6) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. L. Electric Field Modulated Nonlinear Optical Properties of Donor–Acceptor Polyenes: Sum-over-States Investigation of the Relationship between Molecular Polarizabilities ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) and Bond Length Alternation. *J. Am. Chem. Soc.* **1994**, *116*, 10703–10714.

- (7) Tykwinski, R. R.; Gubler, U.; Martin, R. E.; Diederich, F.; Bosshard, C.; Günter, P. Structure-Property Relationships in Third-Order Nonlinear Optical Chromophores. *J. Phys. Chem. B* **1998**, *102*, 4451–4465.

- (8) McDonagh, A. M.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Houbrechts, S.; Wada, T.; Sasabe, H.; Persoons, A. Organometallic Complexes for Nonlinear Optics. 16. Second and Third Order Optical Nonlinearities of Octopolar Alkynylruthenium Complexes. *J. Am. Chem. Soc.* **1999**, *121*, 1405–1406.

- (9) de Melo, C. P.; Silbey, R. Variational-Perturbational Treatment for the Polarizabilities of Conjugated Chains. II. Hyperpolarizabilities of Polyenic Chains. *J. Chem. Phys.* **1988**, *88*, 2567–2571.

- (10) Nakano, M.; Shigemoto, I.; Yamada, S.; Yamaguchi, K. Size-Consistent Approach and Density Analysis of Hyperpolarizability: Second Hyperpolarizabilities of Polymeric Systems with and without Defects. *J. Chem. Phys.* **1995**, *103*, 4175–4191.

- (11) Chen, W.; Li, Z. R.; Wu, D.; Li, Y.; Sun, C. C.; Gu, F. L. The Structure and the Large Nonlinear Optical Properties of Li@calix[4]pyrrole. *J. Am. Chem. Soc.* **2005**, *127*, 10977–10981.

- (12) Ohira, S.; Hales, J. M.; Thorley, K. J.; Anderson, H. J.; Perry, J. W.; Brédas, J. L. A New Class of Cyanine-like Dyes with Large Bond-Length Alternation. *J. Am. Chem. Soc.* **2009**, *131*, 6099–6101.

- (13) Kuzyk, M. G. Physical Limits on Electronic Nonlinear Molecular Susceptibilities. *Phys. Rev. Lett.* **2000**, *85*, 1218–1221.

- (14) Kuzyk, M. G. Erratum: Physical Limits on Electronic Nonlinear Molecular Susceptibilities [Phys. Rev. Lett. 85, 001218 (2000)]. *Phys. Rev. Lett.* **2003**, *90*, 039902(E).

- (15) Nakano, M.; Kishi, R.; Ohta, S.; Takahashi, H.; Kubo, T.; Kamada, K.; Ohta, K.; Botek, E.; Champagne, B. Relationship between Third-Order Nonlinear Optical Properties and Magnetic Interactions in Open-Shell Systems: A New Paradigm for Nonlinear Optics. *Phys. Rev. Lett.* **2007**, *99*, 033001/1–033001/4.

- (16) Nakano, M.; Kishi, R.; Nitta, T.; Kubo, T.; Nakasuji, K.; Kamada, K.; Ohta, K.; Champagne, B.; Botek, E.; Yamaguchi, K. Second Hyperpolarizability ( $\gamma$ ) of Singlet Diradical System: Dependence of  $\gamma$  on the Diradical Character. *J. Phys. Chem. A* **2005**, *109*, 885–891.

- (17) Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasuji, K.; Kishi, R.; Ohta, S.; Furukawa, S.; Takahashi, H.; et al. Strong Two-Photon Absorption of Singlet Diradical Hydrocarbons. *Angew. Chem., Int. Ed.* **2007**, *46*, 3544–3546.

- (18) Cho, S.; Lim, J. M.; Hiroto, S.; Kim, P.; Shinokubo, H.; Osuka, A.; Kim, D. Unusual Interchromophoric Interactions in  $\beta,\beta'$ -Directly and Doubly Linked Corrole Dimers: Prohibited Electronic Communication and Abnormal Singlet Ground States. *J. Am. Chem. Soc.* **2009**, *131*, 6412–6420.

- (19) Kishida, H.; Hibino, K.; Nakamura, A.; Kato, D.; Abe, J. Third-Order Nonlinear Optical Properties of a  $\pi$ -Conjugated Biradical Molecule Investigated by Third-Harmonic Generation Spectroscopy. *Thin Sol. Films* **2010**, *519*, 1028–1030.

- (20) Zeng, Z.; Sung, Y. M.; Bao, N.; Tan, D.; Lee, R.; Zafra, J. L.; Lee, B. S.; Ishida, M.; Ding, J.; Navarrete, J. T. L.; et al. Stable Tetrabenzo-Chichibabin's Hydrocarbons: Tunable Ground State and Unusual Transition between Their Closed-Shell and Open-Shell Resonance Forms. *J. Am. Chem. Soc.* **2012**, *134*, 14513–14525.

- (21) Li, Y.; Heng, W.-K.; Lee, B. S.; Aratani, N.; Zafra, J.; Bao, N.; Lee, R.; Sung, Y. M.; Sun, Z.; Huang, K.-W.; et al. Kinetically Blocked

Stable Heptazethrene and Octazethrene: Closed-Shell or Open-Shell in the Ground State? *J. Am. Chem. Soc.* **2012**, *134*, 14913–14922.

(22) Hayes, E. F.; Siu, A. K. Q. Electronic Structure of the Open Forms of Three-Membered Rings. *J. Am. Chem. Soc.* **1971**, *93*, 2090–2091.

(23) Yamaguchi, K. In *Self-Consistent Field: Theory and Applications*; Carbo, R., Klobukowski, M., Eds.; Elsevier: Amsterdam, 1990; pp 727–828.

(24) Nakano, M.; Fukui, H.; Minami, T.; Yoneda, K.; Shigeta, Y.; Kishi, R.; Champagne, B.; Botek, E.; Kubo, T.; Ohta, K.; et al. (Hyper)polarizability Density Analysis for Open-Shell Molecular Systems Based on Natural Orbitals and Occupation Numbers. *Theor. Chem. Acc.* **2011**, *130*, 711–724.

(25) Nakano, M.; Fukui, H.; Minami, T.; Yoneda, K.; Shigeta, Y.; Kishi, R.; Champagne, B.; Botek, E.; Kubo, T.; Ohta, K.; et al. Erratum to: (Hyper)polarizability Density Analysis for Open-Shell Molecular Systems based on Natural Orbitals and Occupation Numbers. *Theor. Chem. Acc.* **2011**, *130*, 725–726.

(26) Kamada, K.; Ohta, K.; Shimizu, A.; Kubo, T.; Kishi, R.; Takahashi, H.; Botek, E.; Champagne, B.; Nakano, M. Singlet Diradical Character from Experiment. *J. Phys. Chem. Lett.* **2010**, *1*, 937–940.

(27) Lambert, C. Towards Polycyclic Aromatic Hydrocarbons with a Singlet Open-Shell Ground State. *Angew. Chem., Int. Ed.* **2011**, *50*, 1756–1758.

(28) Sun, Z.; Wu, J. Open-Shell Polycyclic Aromatic Hydrocarbons. *J. Mater. Chem.* **2012**, *22*, 4151–4160.

(29) Smith, M. B.; Michl, J. Singlet Fission. *Chem. Rev.* **2010**, *110*, 6891–6936.

(30) Minami, T.; Nakano, M. Diradical Character View of Singlet Fission. *J. Phys. Chem. Lett.* **2012**, *3*, 145–150.

(31) Bendikov, M.; Duong, H. M.; Starkey, K.; Houk, K. N.; Carter, E. A.; Wudl, F. Oligoacenes: Theoretical Prediction of Open-Shell Singlet Diradical Ground States. *J. Am. Chem. Soc.* **2004**, *126*, 7416–7417.

(32) Konishi, A.; Hirao, Y.; Nakano, M.; Shimizu, A.; Botek, E.; Champagne, B.; Shiomi, D.; Sato, K.; Takui, T.; Matsumoto, K.; et al. Synthesis and Characterization of Teranthene: A Singlet Biradical Polycyclic Aromatic Hydrocarbon Having Kekulé Structures. *J. Am. Chem. Soc.* **2010**, *132*, 11021–11023.

(33) Tönshoff, C.; Bettinger, H. F. Photogeneration of Octacene and Nonacene. *Angew. Chem., Int. Ed.* **2010**, *49*, 4125–4128.

(34) Fukui, H.; Inoue, Y.; Yamada, T.; Ito, S.; Shigeta, Y.; Kishi, R.; Champagne, B.; Nakano, M. Enhancement of the Third-Order Nonlinear Optical Properties in Open-Shell Singlet Transition-Metal Dinuclear Systems: Effects of the Group, of the Period, and of the Charge of the Metal Atom. *J. Phys. Chem. A* **2012**, *116*, 5501–5509.

(35) Nakano, M.; Minami, T.; Yoneda, K.; Muhammad, S.; Kishi, R.; Shigeta, Y.; Kubo, T.; Rougier, L.; Champagne, B.; Kamada, K.; et al. Giant Enhancement of the Second Hyperpolarizabilities of Open-Shell Singlet Polyaromatic Diphenalenyl Diradicaloids by an External Electric Field and Donor–Acceptor Substitution. *J. Phys. Chem. Lett.* **2011**, *2*, 1094–1098.

(36) Zhou, Z.-J.; Li, X.-P.; Ma, F.; Liu, Z.-B.; Li, Z.-R.; Huang, X.-R.; Sun, C.-C. Exceptionally Large Second-Order Nonlinear Optical Response in Donor–Graphene Nanoribbon–Acceptor Systems. *Chem.—Eur. J.* **2011**, *17*, 2414–2419.

(37) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

(38) Neto, A. H. C.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K. The Electronic Properties of Graphene. *Rev. Mod. Phys.* **2009**, *81*, 109–162.

(39) Takatsuka, K.; Fueno, T.; Yamaguchi, K. Distribution of Odd Electrons in Ground-State Molecules. *Theor. Chim. Acta.* **1978**, *48*, 175–183.

(40) Head-Gordon, M. Characterizing Unpaired Electrons from the One-Particle Density Matrix. *Chem. Phys. Lett.* **2003**, *372*, 508–511.

(41) Iikura, H.; Tsuneda, T.; Yanai, T.; Hirao, K. A Long-Range Correction Scheme for Generalized-Gradient-Approximation Exchange Functionals. *J. Chem. Phys.* **2001**, *115*, 3540–3544.

(42) Cohen, H. D.; Roothaan, C. C. J. Electric Dipole Polarizability of Atoms by the Hartree–Fock Method. I. Theory for Closed-Shell Systems. *J. Chem. Phys.* **1965**, *43*, S34–S39.

(43) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. A Spin Correction Procedure for Unrestricted Hartree–Fock and Moller–Plesset Wavefunctions for Singlet Diradicals and Polyradicals. *Chem. Phys. Lett.* **1988**, *149*, 537–542.

(44) Pollet, R.; Amara, H. Spin-Unrestricted Calculations of Bare-Edged Nanographenes Using DFT and Many-Body Perturbation Theory. *J. Chem. Theory Comput.* **2009**, *5*, 1719–1722.

(45) Nakano, M.; Minami, T.; Fukui, H.; Yoneda, K.; Shigeta, Y.; Kishi, R.; Champagne, B.; Botek, E. Approximate Spin-Projected Spin-Unrestricted Density Functional Theory Method: Application to the Diradical Character Dependences of the (Hyper)polarizabilities in *p*-Quinodimethane Models. *Chem. Phys. Lett.* **2010**, *501*, 140–145.

(46) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A. et al. *Gaussian 09*, revision B.01; Gaussian, Inc.: Wallingford, CT, 2010.