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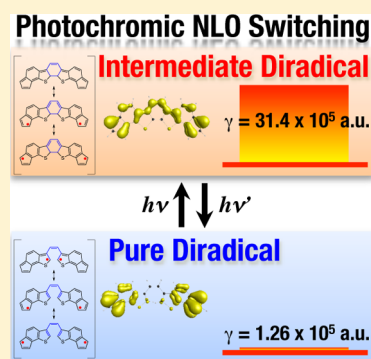
# Photochromic Switching of Diradical Character: Design of Efficient Nonlinear Optical Switches

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**S** Supporting Information

**ABSTRACT:** Open-shell singlet diradical molecules have been widely investigated because they are key to understanding the nature of chemical bonds. We propose a new concept for reversible switching of diradical character—an index of the instability of chemical bonds—of a molecule by photochromic reaction. Photochromic diarylethene derivatives with various open-shell singlet diradical characters are theoretically designed, and their photochromic diradical character switching behaviors are clarified. These results contribute to designing highly efficient third-order nonlinear optical switching substances based on the correlation between the diradical character and second hyperpolarizability.



**SECTION:** Molecular Structure, Quantum Chemistry, and General Theory

Singlet diradical compounds have been widely investigated from both theoretical and experimental researchers because they have peculiar electronic structures and are key to understanding the nature of chemical bonds.<sup>1–10</sup> The diradical nature of a molecule is quantified by the diradical character ( $y$ )—an index of the instability of chemical bonds—ranging from 0 (closed-shell) to 1 (pure diradical),<sup>11,12</sup> so that, in other words,  $1 - y$  indicates an “effective bond order”. Interesting physicochemical properties of singlet diradical compounds are found to originate in the diradical character. Among them, we have theoretically clarified the correlations between the diradical character and excitation energies/properties, and thus have revealed a remarkable enhancement of the second hyperpolarizability ( $\gamma$ ), which is the microscopic origin of third-order nonlinear optical (NLO) property in the intermediate diradical character.<sup>13–15</sup> This theoretical prediction has subsequently been verified by the experimental results of gigantic two-photon absorption cross section, which is proportional to the imaginary part of  $\gamma$ , of the polycyclic aromatic hydrocarbons with intermediate  $y$ .<sup>16–18</sup> Although this new correlation between  $y$  and  $\gamma$  is expected to open a new paradigm for highly efficient NLO materials,<sup>1,14</sup> there are still no reports on the methods for reversible switching or tuning of the  $y$  and  $\gamma$  values except for switching external strong static electric field applied to symmetric open-shell singlet systems,<sup>19</sup> which leads to asymmetric open-shell singlet systems.<sup>20</sup> The development of such reversible tuning method as well as of molecular design of practical compounds would contribute to opening up a new class of highly efficient NLO switching.

As a typical example of such tuning methods of properties through the change of molecular structures, we can consider

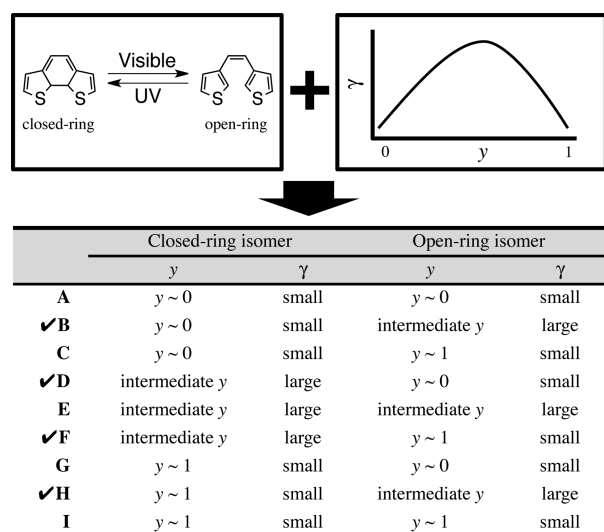
“photochromism”. Photochromism is defined as reversible isomerization between two isomers, where at least one direction of reversible reaction is a photoinduced one.<sup>21–23</sup> Among various photochromic compounds, diarylethene derivatives undergo cyclization and cycloreversion in  $6\pi$ -electrocyclic reactions.<sup>24–26</sup> Through these reactions,  $\pi$ -conjugation length in a molecule can be reversibly changed, where typically the open-ring isomer with less extended  $\pi$ -conjugation is colorless, while the closed-ring isomer with more extended  $\pi$ -conjugation is colored. Following this principle, various diarylethene derivatives with modification of aryl rings have been synthesized.<sup>24–26</sup> In regard to the open-shell diarylethene derivatives, Matsuda and Irie reported that the intramolecular magnetic interaction in high spin states of diarylethene derivatives with nitronyl nitroxide radical sources can reversibly changed along the cyclization and cycloreversion reactions.<sup>27</sup> In sharp contrast to this traditional  $\pi$ -conjugation based principle, we here propose a reversible change scheme of diradical character  $y$ , i.e., the effective bond order, within a range of closed-shell ( $y = 0$ ) and pure diradical ( $y = 1$ ) states by the change of molecular structure through the photochromic reactions, and thus apply this  $y$  tuning method to  $\gamma$  switching by light irradiation.

By combining the photochromic reaction and the diradical character based principle, we propose a new concept for light-induced reversible switching of  $\gamma$  values through tuning  $y$  (Figure 1). There can be nine classes (A–I) of systems, which

**Received:** June 13, 2013

**Accepted:** July 11, 2013

**Published:** July 11, 2013

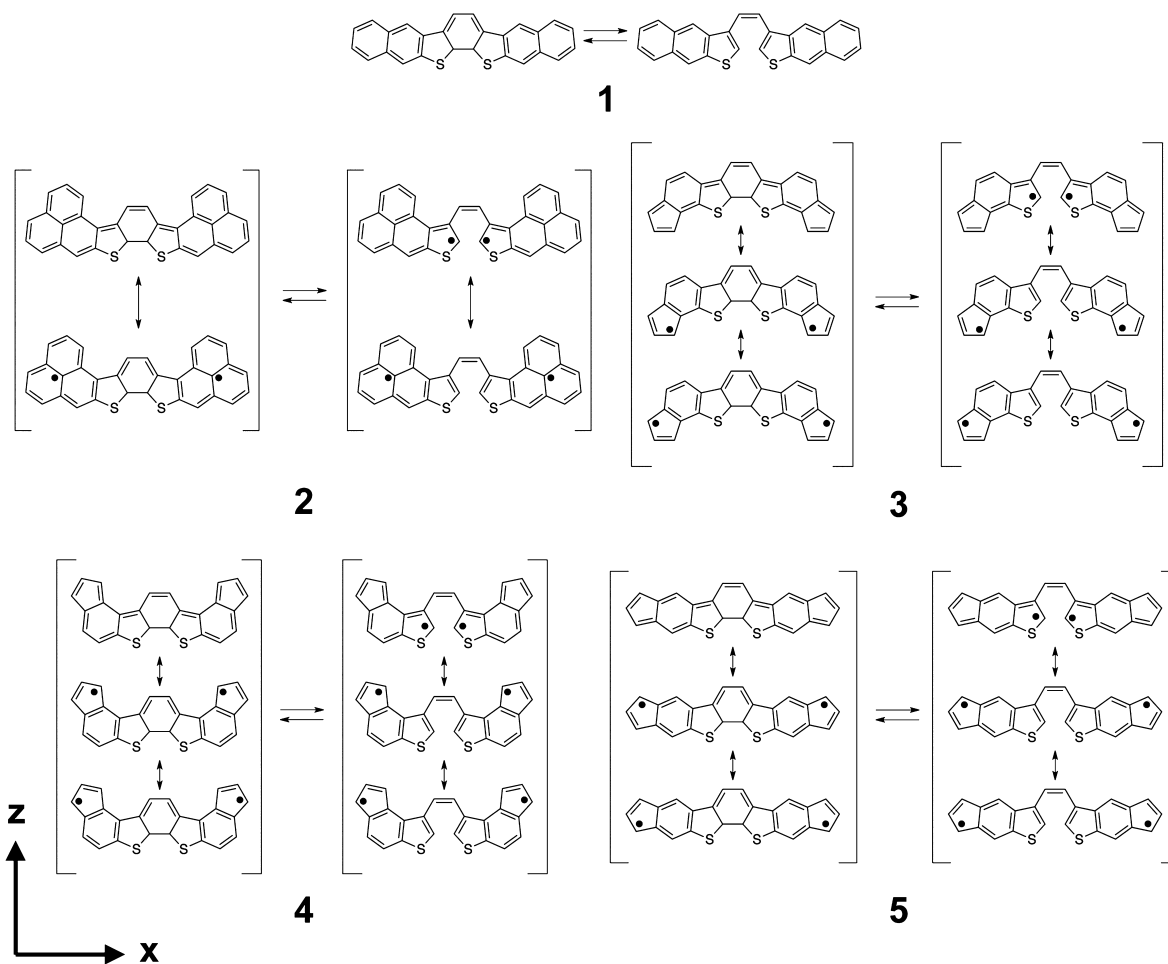


**Figure 1.** Concept for the light-induced reversible switching of diradical character ( $y$ ) and second hyperpolarizability ( $\gamma$ ). Nine classes A–I are shown together with the features of  $y$  and  $\gamma$  for closed- and open-ring isomers. Marked systems (B, D, F, and H) are  $\gamma$  switchable systems.

are categorized by the combination of molecular structures (closed- and open-ring isomers in diarylethene derivatives) and

diradical characters [ $y \sim 0$  (closed-shell),  $0 < y < 1$  (intermediate diradical), and  $y \sim 1$  (pure diradical)]. Class A indicates a conventional system, which has closed-shell state ( $y \sim 0$ ) in both closed- and open-ring isomers, while classes B–I have finite diradical characters in closed- and/or open-ring isomers. It is expected that B, D, F, and H show significant switching property of  $\gamma$  since they take intermediate diradical character (where  $\gamma$  is maximized) in one side of isomers, while they exhibit closed-shell or pure diradical character (where  $\gamma$  is minimized) in the other isomer. Systems with intermediate diradical characters are predicted when two radical sites partially interact with each other. The molecular structure change in photochromic reaction leads to a conjecture that closed-ring isomers prefer to have closed-shell or intermediate diradical character, while open-ring isomers are not expected to have intermediate diradical characters due to the breaking of  $\pi$ -conjugation. Classes B and H are thus excluded for the present purpose. We clarify the difference in  $y$  and  $\gamma$  between closed- and open-ring structures in several diarylethene derivatives by quantum chemical calculations. On the basis of these results, we present a new class of  $\gamma$  switching systems through tuning  $y$  in photochromic reaction.

To verify our concept, we theoretically designed several diarylethene derivatives (Figure 2) with singlet diradical character and clarified the relationship between the  $y$  and longitudinal  $\gamma(\gamma_{xxxx})$  values of these systems by quantum



**Figure 2.** Resonance structures of designed diarylethene derivatives with singlet open-shell diradical characters. Closed- and open-ring isomers are shown on the left- and right-hand sides of arrows, respectively.

chemical calculations. All the calculations were performed with the 6-31+G\* basis set. Geometry optimizations were performed using the spin-unrestricted B3LYP (UB3LYP) method. Diradical characters were evaluated from the occupation numbers of the spin-unrestricted Hartree–Fock (UHF) natural orbitals (NOs). We employed the finite-field (FF) method to the calculation of  $\gamma$  using the LC-UBLYP functional with a range separating parameter  $\mu = 0.33$  bohr<sup>-1</sup>. Computational details are represented in the Supporting Information. Compound **1** presents reference closed-shell systems without any radical resonance structures both in closed- and open-ring isomers. Compounds **2–5** are expected to have diradical characters due to the multiple resonance structures including closed- and open-shell structures, in which open-ring isomers are expected to have pure diradical characters. The thermal stability of these molecules is sufficiently expected because they consist of thermally stable diarylethene backbone and thermally stable diradical moieties such as diphenalenyl rings.<sup>7,8</sup>

Table 1 summarizes the calculated  $y$  and  $\gamma$  values for compounds **1–5**. Their relative amplitudes of  $\gamma$  as well as of

**Table 1.** Diradical Character  $y$  Calculated Using the UHF/6-31+G\* Method and the Longitudinal Component of Second Hyperpolarizability  $\gamma(\gamma_{xxx})$  Calculated Using the LC-UBLYP/6-31+G\* Method for **1–5** in Their Closed- and Open-Ring Isomers (Figure 2)

system	class	closed-ring		open-ring		$\gamma_c/\gamma_o^a$
		$y$	$\gamma/\text{a.u.}$	$y$	$\gamma/\text{a.u.}$	
1	A	0.0000	$3.93 \times 10^5$	0.0000	$7.37 \times 10^4$	5.33
2	C	0.0000	$1.71 \times 10^6$	0.9842	$1.60 \times 10^5$	10.7
3	F	0.6938	$3.14 \times 10^6$	0.9949	$1.26 \times 10^5$	24.9
4	F	0.8353	$1.93 \times 10^6$	0.9963	$5.31 \times 10^4$	26.2
5	I	0.9803	$9.23 \times 10^5$	0.9923	$2.31 \times 10^5$	3.99

<sup>a</sup>Switching ratio, where  $\gamma_c$  and  $\gamma_o$  represents the  $\gamma$  values for closed- and open-ring isomers, respectively.

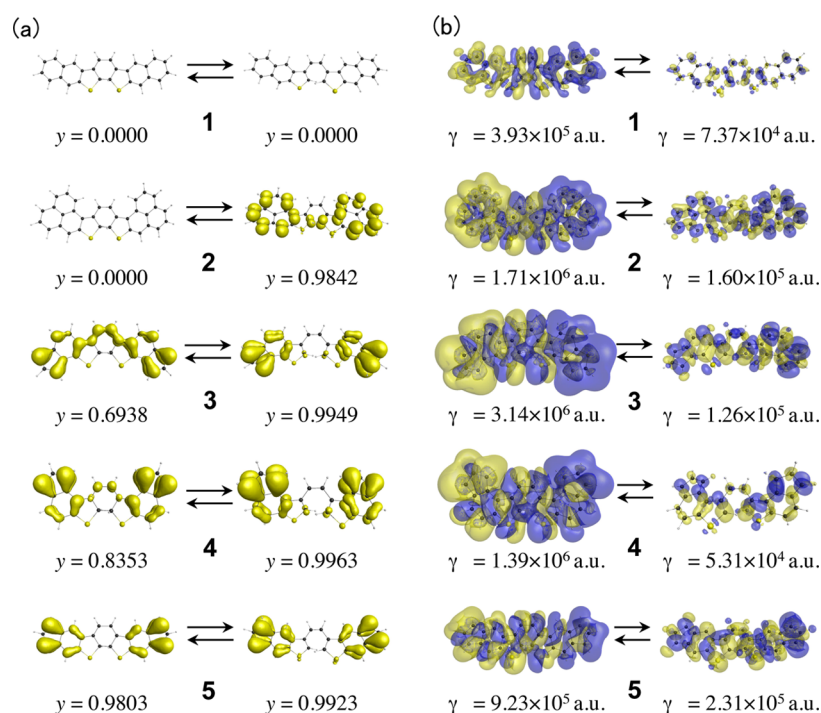
switching ratios are explained as follows based on the  $y$ – $\gamma$  correlation principle and the  $\pi$ -conjugation size. As expected, **1** displays closed-shell character ( $y = 0$ ) in both closed- and open-ring isomers (class A), which thus lead to the relatively small  $\gamma$  values among these systems. For **1**, we therefore predict that the larger  $\gamma$  in the closed-ring isomer than in the open-ring isomer is caused by only the more extended  $\pi$ -conjugation in the closed-ring isomer. This results in a fairly small switching ratio ( $\gamma_c/\gamma_o = 5.33$ ). For **2**, we also observe a relatively small switching ratio (10.7) though the open-shell nature is drastically changed between closed- and open-ring isomers. This is ascribed to the fact that both isomers—closed-shell and nearly pure open-shell states (class C), respectively—do not maximize  $\gamma$  based on the  $y$ – $\gamma$  correlation. Namely, similar to **1**, the relatively small switching ratio is predicted to be primarily caused by the larger  $\pi$ -conjugation size in the closed-ring isomer than in the open-ring isomer. In contrast, it is found that **3** and **4** are switched from intermediate diradical systems in the closed-ring isomers to pure diradical systems in the open-ring isomers (class F). It is found that the intermediate diradical characters in the closed-ring isomers cause the significantly larger closed-ring  $\gamma$  values of **3** and **4** as compared to **1**, i.e.,  $\gamma_c(\mathbf{3})/\gamma_c(\mathbf{1}) \approx 8.0$  and  $\gamma_c(\mathbf{4})/\gamma_c(\mathbf{1}) \approx 4.9$ , whereas the pure diradical characters in the open-ring isomers of **3** and **4** cause the small  $\gamma$  values similar to that of **1** (closed-shell). Therefore, the switching ratios of **3** (24.9) and **4** (26.2) are shown to be

significantly larger than that of **1** (5.33). On the other hand, it turns out that **5** shows nearly pure diradical characters in both the closed- and open-ring isomers, which lead to their relatively small  $\gamma$  values as well as the smallest switching ratio (3.99) among these systems. Among the nonswitching classes, A, C, and I, categorized in Figure 2, the present compounds show the relative amplitudes of  $\gamma$ -switching ratios: **2** (class C) > **1** (class A)  $\sim$  **5** (class I), which is primarily caused by the  $\pi$ -conjugation over the both-end rings in the closed-ring isomer of **2** (due to involving phenalenyl rings at both ends) larger than of **1** and **5** (for details, see the Supporting Information). To further investigate these relationships, we next clarify the spatial electron contribution to  $y$  and  $\gamma$  values in closed- and open-ring isomers.

The spatial contribution of unpaired (odd) electrons to diradical character can be analyzed by the odd electron density distribution.<sup>28,29</sup> Figure 3a shows the odd electron density distributions of **1–5** together with their  $y$  values. In closed-shell ( $y = 0$ ) systems, i.e., the closed- and open-ring isomers of **1** and closed-ring isomer of **2**, there are no odd electrons in the molecules. In open-shell ( $y > 0$ ) systems,  $\pi$  electrons are shown to primarily contribute to the odd electron density distributions. In pure diradical systems ( $y \sim 1$ ), i.e., closed-ring isomer of **5**, and open-ring isomers of **2–5**, odd electron distributions are shown to be well localized on the left- and right-hand sides of the molecules, while in intermediate diradical systems, i.e., the closed-ring isomers of **3** and **4**, the odd electron density distributions exhibit some extension to the ethene bridges. The amplitudes and spatial distribution features of odd electron densities of **1–5** are also found to be in qualitative agreement with those expected from their resonance structures shown in Figure 2, where the systems with the contributions of both the closed-shell and diradical resonance structures, i.e., the closed-ring isomers of **2–5**, are expected to be intermediate and pure diradical systems except for the closed-ring isomer of **2** (closed-shell). For quantitative estimation of diradical character, the broken symmetry (BS) quantum chemical method is known to be a useful tool because the diradical character ( $y$ ;  $0 \leq y \leq 1$ ) is defined as the occupation number of the lowest unoccupied natural orbitals.<sup>13,28</sup> Since the odd electron density can illustrate the spatial distribution of unpaired electrons and is directly related to the diradical character,<sup>28</sup> the odd electron density distribution is useful for fine-tuning the diradical characters of molecules through the choice of substituents, structural modifications of both-end moieties and so forth. According to the above discussion, a prescription for designing closed-ring systems with intermediate diradical character is described as follows:

1. Design the closed-ring systems having both closed-shell and diradical resonance structures.
2. Perform BS calculation of the diradical character as well as the odd electron densities.
3. Adopt the systems with intermediate diradical characters, which are characterized by the moderately delocalized odd electron density distributions.

Figure 3b shows the  $\gamma$  density distributions of compounds **1–5**. The positive and negative  $\gamma$  densities multiplied by the cubed field amplitude correspond to the field-induced increase and decrease in the third-order charge density, respectively, and create the third-order dipole moment (third-order polarization) in the direction from positive to negative  $\gamma$  density. Therefore, the  $\gamma$  density map represents the relative phase and amplitudes



**Figure 3.** Odd electron density distributions corresponding the diradical character  $\gamma$  calculated using the UHF/6-31+G\* method (a) as well as  $\gamma$  density distributions (b) calculated using the LC-UBLYP/6-31+G\* method of 1–5. In (a), the yellow surfaces represent the densities with isosurface with 0.0015 a.u., while in (b), the yellow and blue surfaces represent the positive and negative  $\gamma$  densities, respectively, with isosurface with  $\pm 100$  a.u. In both (a) and (b), closed- and open-ring isomers are shown on the left- and right-hand sides of arrows, respectively.

of the change in the third-order charge densities between two spatial points with positive and negative  $\gamma$  densities. In all systems, the main contributions to  $\gamma$  are shown to originate from the  $\pi$  electron third-order polarization. Moreover, the domains with primary  $\gamma$  density distributions are found to correspond to those with significant odd electron density distributions particularly in the intermediate diradical character region. This suggests that the electrons with an intermediate diradical character contribute to the enhancement of  $\gamma$  value. For the closed-ring isomers of 2, 3, and 4, the primary positive contributions to  $\gamma$  are shown to come from the extended positive and negative  $\gamma$  densities well separated on the left- and right-hand sides of the molecules, respectively. In particular, the significant extension of  $\gamma$  densities of 3 and 4 in the closed-ring isomers is predicted to originate in their intermediate diradical characters as observed in our previous studies.<sup>30–32</sup> On the other hand, the small  $\gamma$  values of 1 and 5 as well as of the open-ring isomers for all systems are exemplified by the substantial reduction of the  $\gamma$  density amplitudes.

To summarize, we demonstrate a novel concept that diradical character  $\gamma$  and thus the second hyperpolarizability  $\gamma$  can be tuned through the photochromic reaction in some diarylethene derivatives based on the diradical character based design principle for open-shell singlet NLO systems. The change in  $\gamma$  values between the closed- and open-ring isomers is found to be quantitatively predictable based on the resonance structures, which enable us to design molecules with desired change of  $\gamma$  and thus of  $\gamma$  in the photochromic reaction. This result paves the way for designing the highly efficient NLO switch based on the open-shell singlet photochromic molecules.

## ■ ASSOCIATED CONTENT

### Supporting Information

Computational details, relative amplitudes of  $\gamma$ -switching ratios for 1, 2 and 5, and the geometries of calculated molecules. This 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.

## ■ ACKNOWLEDGMENTS

This work is supported by Grant-in-Aid for Scientific Research (Nos. 25248007, 22685003, 24750017) from the Japan Society for the Promotion of Science (JSPS), a Grant-in-Aid for Scientific Research on Innovative Areas “Stimuli-responsive Chemical Species” (No. A24109002a), MEXT, the Strategic Programs for Innovative Research (SPIRE), MEXT, and the Computational Materials Science Initiative (CMSI), Japan. K.O. expresses his special thanks for a JSPS Research Fellowship for Young Scientists. Theoretical calculations were partly performed using the Research Center for Computational Science, Okazaki, Japan.

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