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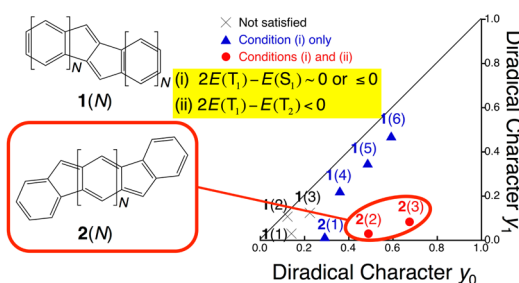
Diradical Character Based Design for Singlet Fission of Condensed-Ring Systems with  $4n\pi$  Electrons

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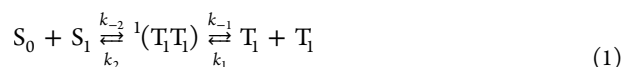
## Supporting Information

**ABSTRACT:** By applying the diradical character based molecular design guideline for singlet fission (SF), we investigate the feasibility of efficient SF in condensed-ring  $\pi$ -conjugated molecules with  $4n\pi$  electrons ( $n = 4, 5, \dots$ ), i.e., antiaromatic polycyclic hydrocarbons composed of five- and six-membered rings. The multiple diradical character ( $y_i$ ), which takes a value between 0 (closed shell) and 1 (pure open shell), is defined as the occupation number of the lowest unoccupied natural orbital (LUNO) +  $i$  ( $i = 0, 1, \dots$ ) calculated using the approximately spin-projected spin-unrestricted Hartree–Fock method. The excitation energies are also evaluated using the tuned long-range corrected time-dependent density functional theory method with the Tamm–Dancoff approximation to examine the energy level matching conditions for SF: (i)  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$  and (ii)  $2E(T_1) - E(T_2) < 0$ , where  $S_1$ ,  $T_1$  and  $T_2$  represent singlet first, triplet first, and triplet second excited states, respectively. It turns out that the energy level matching conditions are satisfied in relatively small-size antiaromatic condensed-ring molecules with  $y_0 \sim 0.4$  and  $y_1/y_0 < 0.2$ , i.e., intermediate diradical character without significant tetraradical character. This finding also demonstrates the reliability of our design guidelines presented in our previous study.

4n $\pi$  Condensed-Ring Molecules for Singlet Fission

## 1. INTRODUCTION

Recently, a lot of efforts have been devoted to the improvement of the limit of energy conversion efficiency of photovoltaic cells.<sup>1–5</sup> In organic photovoltaics, an exciton (an electron–hole pair) created by the absorption of photons with threshold energy  $E_{th}$  in chromophores diffuses to the donor/acceptor interface and separates into an isolated electron and hole, which generates an electric current. There are several reasons for limiting the conversion efficiency: (1) photons with the energy below  $E_{th}$  are not absorbed, (2) the excess energy beyond  $E_{th}$  is wasted as heat, (3) some excitons are deactivated before separating into isolated electrons and holes, (4) an exciton–exciton annihilation, etc. The problems (1) and (2) can be solved by using two gap tandem devices, and (3) is improved by using singlet fission (SF),<sup>6–18</sup> resulting in the rise of the theoretical efficiency limit up to 47.7%.<sup>6</sup> Singlet fission is a sort of multiexciton generation (MEG) process,<sup>19</sup> where the chromophores in the excited state with energy higher than  $E_{th}$  distribute their energy to their neighborhood to generate multiple excitons. Although the multiple excitons generated in the MEG process are usually singlet excitons, those in the SF process are triplet excitons. The SF process is approximately described as<sup>7</sup>



where  $S_0$ ,  $S_1$ , and  $T_1$  represent singlet ground state, singlet first excited state, and triplet first excited state of each chromophore, respectively. In the SF process, the threshold energy is equal to  $E(S_1)$  (singlet first excitation energy) and shares its energy with its neighboring chromophores to generate two triplet excitons with energy  $E(T_1)$  (triplet first excitation energy). Since the first step of SF in eq 1 is the spin-allowed process, it occurs very fast in the subpicosecond or picosecond time scale, which is, for example, observed by the absorption of the  $T_1$  state to the higher triplet state  $T_2$  in the pentacene single crystal.<sup>12,13</sup> This time scale is less than that of typical intersystem crossing originating in the spin–orbit coupling. Since the  $T_1$  to  $S_0$  transition is spin-forbidden, triplet excitons have longer lifetimes than those of singlet excitons; i.e., triplet excitons can diffuse over a long distance<sup>20</sup> before deactivation. This feature increases the number of charge separation events at the interface relative to the case of singlet excitons except for the case of a high concentration of triplet excitons, probably causing the triplet–triplet annihilation, where the collision of two triplet excitons generates a higher excited triplet and  $S_0$ , etc.

In the MEG process including SF, the energy of the chromophore in the excited state is lost by sharing it with neighboring chromophores to create lower energy excitons. In

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SF with favorable condition of  $E(S_1) \geq 2E(T_1)$ , the energy loss in the fission from  $S_0 + S_1$  to  $T_1 + T_1$  is represented by  $E(S_1) - 2E(T_1)$ . On the other hand, in the case of  $E(S_1) - 2E(T_1) < 0$ , this magnitude corresponds to the activation energy of SF. To reduce the energy loss or activation energy for SF, we need to search for relevant chromophores which satisfy (i)  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$ .<sup>7</sup> There is another energy condition for efficient SF, (ii)  $2E(T_1) - E(T_2) < 0$ , which is required in order to avoid the recombination of two triplet excitons, generating a higher triplet exciton.<sup>7</sup> These conditions (i) and (ii) have been predicted to be closely related to the multiple diradical character  $y_i$ ,<sup>21</sup> which takes a value between 0 (closed shell) and 1 (pure open shell). The  $y_0$  and  $y_1$  ( $y_0 \geq y_1$ ) values characterize the open-shell nature of tetraradical systems and are also found to closely relate to the excitation energies and transition properties as shown in the nonlinear optical (NLO) responses of open-shell singlet molecules.<sup>22</sup> Indeed, our previous study using the full configuration interaction model of linear  $H_4$  systems has clarified that molecules with finite but relatively small  $y_0$  ( $> 0.1$ ) and  $y_1 \neq y_0$  are suitable for efficient SF.<sup>17</sup> This result implies that small/intermediate diradical molecules without significant tetraradical character are promising candidates for efficient SF. Indeed, the diradical characters of several real SF molecules, e.g., tetracene, pentacene, and 1,3-diphenylisobenzofuran, have been shown to belong to this feasibility region of  $y_i$ .<sup>17</sup> On the other hand, recent theoretical and experimental studies open a novel fascinating field of open-shell singlet condensed-ring  $\pi$ -conjugated systems, e.g., polycyclic aromatic hydrocarbons and graphenes, which exhibit unique physico-chemical properties applicable to future electronics, photonics, and spintronics.<sup>23</sup> Such properties are found to originate in the “open-shell singlet” electronic structures characterized by finite values of diradical characters as well as the odd electron densities<sup>21b,24</sup> on the zigzag edges.<sup>25</sup> For example, it has been demonstrated that the diradical molecules with intermediate diradical characters, i.e., diradicaloids, exhibit prominent enhancement of NLO responses as compared to closed-shell and pure open-shell molecules.<sup>22,25</sup> It has also been predicted that weak aromaticity or antiaromaticity tends to increase the diradical character.<sup>26</sup> In this study, we therefore investigate the feasibility conditions for SF of  $4n\pi$  electron condensed-ring hydrocarbons with different size ( $n = 4, 5, \dots$ ) involving pentalene and dicyclopenta-fused acene core structures based on the diradical characters  $y_0$  and  $y_1$ . From the comparison between these diradical characters and the energy level matching conditions of monomers using the singlet and triplet vertical excitation energies concerned with SF obtained from time-dependent density functional theory (TDDFT) calculations, we discuss the applicability of our diradical character based molecular design guideline for SF and also present promising candidates for SF based on antiaromatic condensed-ring  $\pi$ -conjugated molecules.

## 2. RELATIONSHIP BETWEEN DIRADICAL CHARACTER AND SINGLET FISSION

We briefly explain the relationship between diradical character and excitation energies as well as the diradical character view of feasibility condition of singlet fission.<sup>17</sup> The diradical character  $y_i$ , which is interpreted as the instability in chemical bonds, is defined as  $n_{\text{LUNO}+i}$  [the occupation number of the lowest unoccupied natural orbital (LUNO) +  $i$  ( $i = 0, 1, \dots$ )].<sup>21</sup> In the spin-unrestricted single determinant scheme,  $y_i$  is also represented by  $2 - n_{\text{HONO}-i}$  where  $n_{\text{HONO}-i}$  indicates the

highest occupied natural orbital (HONO) -  $i$  ( $i = 0, 1, \dots$ ).<sup>27</sup> Namely, the  $y_i$ , which takes a value between 0 (closed-shell) and 1 (pure open-shell), represents the diradical nature of  $\alpha$  and  $\beta$  electrons with mutually antiparallel spins described by bonding (HONO- $i$ ) and antibonding (LUNO+ $i$ ) orbital pairs in the singlet wavefunction. For example, when the systems have nonzero  $y_0 \sim y_1$  but negligible  $y_i$  ( $i \geq 2$ ), they are referred to as “tetraradical”, where the four electrons in two pairs of (HONO- $i$ , LUNO+ $i$ ) ( $i = 0, 1$ ) have radical characters, respectively, and the system tends to be more reactive and unstable in the case of larger  $y_i$  values.

The nature of the ground and excited states as well as the excitation energies of open-shell singlet systems are known to be closely related to the diradical character.<sup>28</sup> On the basis of the valence configuration interaction (VCI) model using the symmetric two-site diradical system ( $A^\bullet-B^\bullet$ ),<sup>22a,29</sup> we obtain four electronic states including three singlet and one triplet states. These four states are composed of an essentially neutral (covalent) singlet ground state with gerade (g) symmetry ( $S_0$ ), an ionic singlet state with ungerade (u) symmetry ( $S_1$ ), another singlet state of g symmetry but essentially ionic ( $S_2$ ), and a purely neutral (covalent) triplet state ( $T_1$ ).<sup>22a,29</sup> The relative energies and transition moments of these four states are found to be closely related to the diradical character.<sup>22a</sup> Namely, as increasing  $y_0$  from 0 to 1, the excitation energies of  $S_2$  and  $S_1$ , i.e.,  $E(S_2)$  and  $E(S_1)$ , are found to decrease and then to coincide with each other at the limit of  $y_0 \rightarrow 1$ , while the energy of the  $T_1$  state,  $E(T_1)$  [which is near to  $E(S_1)$  for  $y_0 \sim 0$ ], is found to decrease and to be finally close to that of the singlet ground state ( $S_0$ ) at the limit of  $y_0 \rightarrow 1$  in the case of the negligible exchange integral between the two localized natural orbitals. This is the reason why one focuses on the open-shell singlet systems, which possibly satisfy the feasibility conditions of efficient SF based on the energy level matching, i.e.,  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$ ,<sup>7</sup> in the case of small/intermediate diradical character. On the other hand, in the case of pure diradical systems, most of the absorbed photon energy is wasted as heat in the process of SF since  $2E(T_1)$  is much smaller than  $E(S_1)$ . Thus, the molecules suitable for SF are expected to be designed by tuning the diradical character through chemical modifications. To reveal the relationship between the diradical character and molecular structure, we investigate the analytical expression of diradical character  $y_0$  for the two-site model<sup>22a</sup>

$$y_0 = 1 - \frac{1}{\sqrt{1 + (U/4t)^2}} \quad (2)$$

Here,  $U$  is the difference between on- and inter-site Coulomb repulsions, and  $t$  is a transfer integral, where  $2|t|$  is equal to the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). As seen from eq 2, the diradical character is enhanced in the case of a small HOMO–LUMO gap, which could be realized, for example, in weak aromatic or antiaromatic molecules.<sup>26</sup>

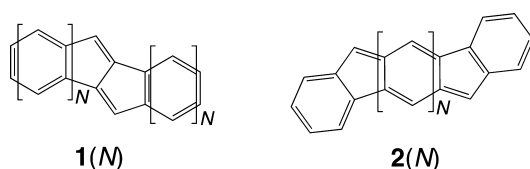
To also examine the singlet dark (even parity) excited state composed of two triplet excitons,  $^1(T_1T_1)$ ,<sup>30</sup> and another triplet state ( $T_2$ ), we need to investigate tetraradical systems. On the basis of a simple tetraradical system, i.e., linear  $H_4$  model, using the full configuration interaction method,<sup>17,22b</sup> we have clarified the correlation between multiple diradical characters ( $y_0, y_1$ ) and the SF feasibility conditions, (i)  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$  and (ii)  $2E(T_1) - E(T_2) < 0$ . It has been found that the

diradical characters suited for SF lie in the region with  $y_0 > 0.10$  except for  $y_0 \sim y_1$ , though its energy efficiency is better in the case of smaller  $y_0$ .<sup>17</sup> Thermally stable diradicaloid and multiradicaloid compounds with small/intermediate diradical characters such as open-shell singlet polycyclic aromatic hydrocarbons<sup>23a,b</sup> are expected to belong to this region and thus to be possible candidates for SF.

### 3. MODEL SYSTEMS AND COMPUTATIONAL METHODS

**3.1.  $4n\pi$  Electron Condensed-Ring Systems.** We here investigate two types of  $4n\pi$  electron condensed-ring hydrocarbons, **1**( $N$ ) ( $N = 1-3$ ) and **2**( $N$ ) ( $N = 1-6$ ). The former and latter involve pentalene and dicyclopenta-fused acene core structures, respectively (Scheme 1). According to Hückel's

**Scheme 1.** Structures of Condensed-Ring Molecules, **1**( $N$ ) and **2**( $N$ ), Where  $N$  Indicates the Number of Fused Rings

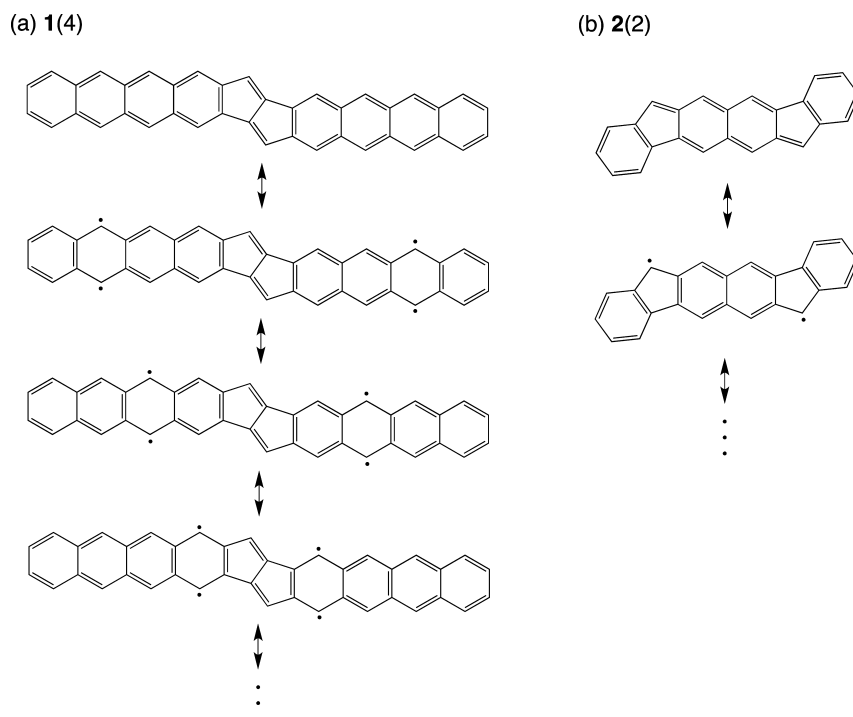


theory, most of  $4n\pi$  electron condensed-ring hydrocarbons, formally referred to as “antiaromatic systems”, have degenerate HOMO and LUMO energies. As pointed out in previous studies,<sup>22a,26</sup> the open-shell character is correlated with the HOMO–LUMO gap, so that  $4n\pi$  electron condensed-ring hydrocarbons are predicted to present open-shell characters and thus to have small  $E(S_1)$  and  $E(T_1)$ . However, most of the condensed-ring conjugated molecules exhibiting SF are known to be  $(4n + 2)\pi$  electron aromatic systems<sup>11–14</sup> and

carotenoids,<sup>15,16</sup> while there have been few reports on SF in  $4n\pi$  electron antiaromatic condensed-ring systems.

With increasing  $N$ , the fused-ring (polyacene) structures are elongated on both sides of central pentalene for **1**( $N$ ) and on the central region for **2**( $N$ ). These molecules are expected to exhibit open-shell characters since polyacene structures are theoretically predicted to present diradical and multiradical (beyond diradical) characters with increasing size.<sup>25b,31</sup> These two types of structures are predicted to present different open-shell characters: with increasing  $N$ , **1**( $N$ ) tends to exhibit tetraradical characters ( $N \geq 2$ ) since it has two polyacene structures on both sides of the pentalene core, while **2**( $N$ ) has a primary diradical character for small  $N$  ( $\leq 3$ ), which is represented by the radical sites on the both-side five-membered rings due to the  $p$ -quinoid–diradical resonance forms in the middle fused-ring region (Figure 1). Molecules **1**( $N$ ) ( $N \geq 2$ ) and **2**( $N$ ) ( $N \leq 3$ ) are therefore expected to be classified as the tetraradical and diradical molecules, only the latter of which are predicted as the candidates for SF based on the molecular design guideline proposed in our previous study.<sup>17</sup> By comparing these model systems, we aim to highlight the difference between diradical and tetraradical molecular systems in application to SF. It is here noted that **1**(1), **1**(2) and **2**(1) as well as their derivatives have been already synthesized because of relatively small open-shell characters, indicating less reactive,<sup>32,33</sup> while there have been no reports on SF in these systems.

**3.2. Computational Details.** Molecular geometries were optimized using the UB3LYP/6-311G\* method under the constraint of symmetry:  $C_{2h}$  for both **1**( $N$ ) ( $N = 1-6$ ) and **2**( $N$ ) ( $N = 1-3$ ). Although one might be concerned about the reliability of the molecular geometry optimized by the spin-unrestricted DFT method and its effect on the obtained results including the diradical character,<sup>34</sup> we have confirmed that the UB3LYP and CASSCF optimized geometries give qualitatively



**Figure 1.** Closed-shell and open-shell resonance structures of **1**(4) (a) and **2**(2) (b).

**Table 1.** Tuned  $\mu$  Values [ $\text{bohr}^{-1}$ ], Diradical Characters ( $y_0, y_1$ )<sup>a</sup> [–], and Excitation Energies [ $E(S_1), E(T_1), E(T_2)$ ]<sup>b</sup> [eV] for Molecules 1(N) and 2(N)

	1(N)						2(N)		
	N = 1	2	3	4	5	6	1	2	3
$\mu$	0.234	0.194	0.172	0.170	0.161	0.157	0.210	0.196	0.185
$y_0$	0.144	0.127	0.227	0.363	0.488	0.595	0.295	0.491	0.678
$y_1$	0.027	0.104	0.122	0.220	0.346	0.469	0.014	0.027	0.081
$E(S_1)$	2.643	2.883	2.756	2.607	2.297	2.033	2.283	2.140	1.975
$E(T_1)$	1.961	1.982	1.818	1.507	1.121	0.831	1.206	0.640	0.115
$E(T_2)$	2.200	2.282	1.996	1.621	1.188	0.868	1.805	1.776	1.507

<sup>a</sup>Obtained, respectively, from eq 5 using the PUHF occupation numbers of LUNO and LUNO+1. <sup>b</sup>Calculated using the TDA/TDDFT scheme with the tuned LC-RBLYP/6-31G\* method.

the same results in the energy level matching conditions for 2(N) (see Tables 10S and 11S in the Supporting Information). We employ the TDDFT method with the Tamm–Dancoff approximation (TDA)<sup>35</sup> to evaluate the relative excitation energies of singlet and triplet states since the TDA/TDDFT scheme is known to significantly remedy the triplet instability problem giving too low or negative triplet excitation energy  $E(T_1)$ .<sup>36</sup> To highlight the effect of the TDA, the excitation energies for 1(N) and 2(N) calculated using the TDA/TDDFT method are compared with those using the TDDFT method in Tables 12S–14S in the Supporting Information. We also adopt the long-range corrected spin-restricted BLYP (LC-RBLYP) functional.<sup>37</sup> This method is known to significantly improve poor descriptions of the conventional DFT for electronic excitation spectra using range-separated hybrids, where the exchange is split into long-range (LR) and short-range (SR) parts by separating the interelectronic distance  $r_{12}$ , e.g., via the use of a range separating parameter  $\mu$  in the standard error function

$$\frac{1}{r_{12}} = \frac{1 - \text{erf}(\mu r_{12})}{r_{12}} + \frac{\text{erf}(\mu r_{12})}{r_{12}} \quad (3)$$

where the first term, corresponding to SR interaction, is described by a modified conventional DFT exchange functional, while the second term, corresponding to LR interaction, is handled by the exact Hartree–Fock (HF) exchange. The range separating parameter  $\mu$  was chosen as  $0.33 \text{ bohr}^{-1}$  using empirical fitting,<sup>37</sup> while the nonempirically tuning scheme of  $\mu$  has been proposed recently by Baer et al. since the relevant  $\mu$  values are found to be strongly dependent on the system.<sup>38a,b</sup> Optimally tuned LC-TDDFT calculations have succeeded in good reproduction of excitation energies for various molecules obtained by experiments and/or by highly electron-correlated calculations.<sup>38c–f</sup> In the approach developed by Baer et al.,  $\mu$  is determined such that the system satisfies a fundamental DFT requirement: in exact Kohn–Sham theory, the negative of the HOMO energy ( $\varepsilon_{\text{HOMO}}$ ) is equal to the ionization potential (IP), i.e.

$$\text{IP}(M) = -\varepsilon_{\text{HOMO}}(M) \quad (4)$$

where  $M$  is the number of electrons of the system. In this study, therefore, the nonempirically tuned LC-RBLYP functional was employed since the target molecules have different structures and size.

The diradical character is evaluated using the approximate spin-projected spin-unrestricted Hartree–Fock (PUHF) as<sup>27</sup>

$$y_i = n_{\text{LUNO}+i}^{\text{ASP}} = 1 - \frac{2T_i}{1 + T_i^2},$$

$$\text{where } T_i = \frac{n_{\text{HONO}-i}^{\text{NSP}} - n_{\text{LUNO}+i}^{\text{NSP}}}{2} \quad (5)$$

Here  $n_k^{\text{ASP}}$  and  $n_k^{\text{NSP}}$  indicate, respectively, the approximate- and non-spin-projected occupation numbers of the corresponding natural orbital  $k$  obtained from UHF calculations. Although the UHF method often overshoots the diradical characters<sup>39</sup> due to the spin contamination, this approximate spin-projection scheme<sup>21</sup> for the UHF occupation numbers is found to well reproduce the diradical characters at the highly electron-correlated level of theory such as the UCCSD and UNO-CASSCF (see Figure 1S in ref 40). The  $y_0$  and  $y_1$  are employed in this study because of investigating tetraradical systems for SF. The features of  $y_0$  and  $y_1$  are also known to be understood by the spatial distributions of odd electron densities.<sup>21b,24</sup> The odd electron density  $D_k^{\text{odd}}(\mathbf{r})$  of the  $k$ th NOs  $\phi_k(\mathbf{r})$  is defined as<sup>24b</sup>

$$D_k^{\text{odd}}(\mathbf{r}) = \min(2 - n_k, n_k) \phi_k^*(\mathbf{r}) \phi_k(\mathbf{r}) \quad (6)$$

where  $\min(2 - n_k, n_k)$  ( $n_k$ : occupation number of the  $k$ th NO) can be regarded as the probability of the electron to be unpaired in  $\phi_k(\mathbf{r})$ . The odd electron density  $D_{y_i}^{\text{odd}}(\mathbf{r})$  for  $y_i$  is expressed within single-determinant schemes as<sup>21b</sup>

$$D_{y_i}^{\text{odd}}(\mathbf{r}) = D_{\text{HONO}-i}(\mathbf{r}) + D_{\text{LUNO}+i}(\mathbf{r}) \quad (7)$$

where  $y_i = \int [D_{y_i}^{\text{odd}}(\mathbf{r})/2] d_3\mathbf{r}$ . This density  $D_{y_i}^{\text{odd}}(\mathbf{r})$  clarifies the spatial contribution of odd electrons to diradical character  $y_i$ .

The 6-31G\* basis set was used for the calculations of diradical characters, odd electron densities, and excitation energies. All the calculations were performed by Gaussian 09<sup>41</sup> and GAMESS<sup>42</sup> program packages.

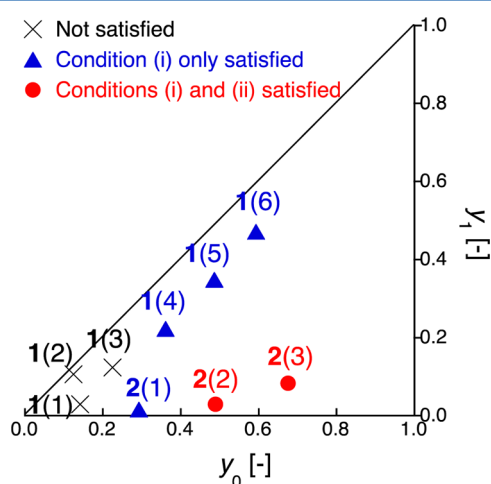
## 4. RESULTS AND DISCUSSION

**4.1. Correlation between Diradical Character and Molecular Structure.** Table 1 lists the tuned  $\mu$  values, multiple diradical characters ( $y_0$  and  $y_1$ ), and excitation energies [ $E(S_1)$ ,  $E(T_1)$ , and  $E(T_2)$ ]. The oscillator strengths for  $S_0 \rightarrow S_n$  transitions are listed in Table 15S in the Supporting Information. Before discussing the correlation between the diradical character and molecular structure, we examine the relationship between the tuned range separating parameter  $\mu$  ( $\text{bohr}^{-1}$ ) and the  $\pi$ -conjugated lengths of these molecules. In this study, we obtained tuned  $\mu$  values for each system by averaging  $\mu$  values obtained by imposing eq 4 for the HOMOs of neutral (with  $M$  electrons) and anion (with  $M + 1$  electrons) states of each system. The results are listed in Table 1, which



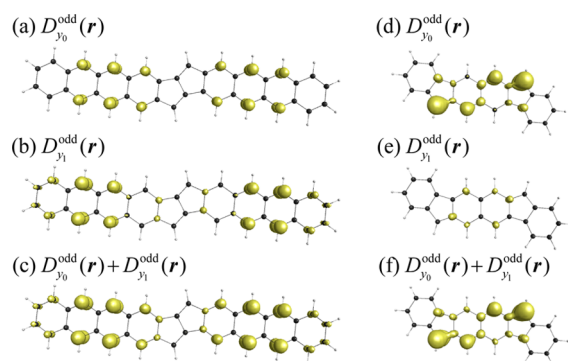
shows the order of  $\mu^{-1}$  in amplitude:  $1(1) < 2(1) < 2(2) < 1(2) < 2(3) < 1(3) < 1(4) < 1(5) < 1(6)$ . This feature—the systems having longer  $\pi$ -conjugated lengths exhibit the larger tuned  $\mu^{-1}$ —exemplifies that  $\mu^{-1}$  is an effective indicator of delocalization size.<sup>43</sup>

The classification based on the diradical characters is found to be useful for understanding the relationship between molecular structures and the excitation energies.<sup>17,26b,44</sup> In general, open-shell singlet molecules for singlet fission are found to be classified into three groups:<sup>17</sup> (I) nearly closed-shell systems with negligible ( $y_0, y_1$ ) (in the vicinity of the origin), (II) diradical systems having finite  $y_0$  but negligible  $y_1$  (in the vicinity of  $y_0$  axis), and (III) tetraradical systems having finite  $y_0$  and  $y_1$  including genuine tetraradical systems with  $y_1 \sim y_0$  [in the vicinity of the diagonal ( $y_0 = y_1$ ) line]. Figure 2 and



**Figure 2.** Diradical characters  $y_0$  and  $y_1$  of  $1(N)$  ( $1 \leq N \leq 6$ ) and  $2(N)$  ( $1 \leq N \leq 3$ ). Black cross, blue triangle, and red circle indicate the systems, which do not satisfy both conditions (i) and (ii), satisfy only condition (i), and satisfy both conditions (i) and (ii), respectively.

Table 1 show the diradical characters ( $y_0, y_1$ ) of  $1(N)$  and  $2(N)$ . First, we examine the spatial features of open-shell characters of these systems using odd electron densities (eq 7) to clarify the relationship between the open-shell characters and their molecular structures. Figure 3 shows  $D_{y_i}^{\text{odd}}(\mathbf{r})$  ( $i = 0, 1$ ) and



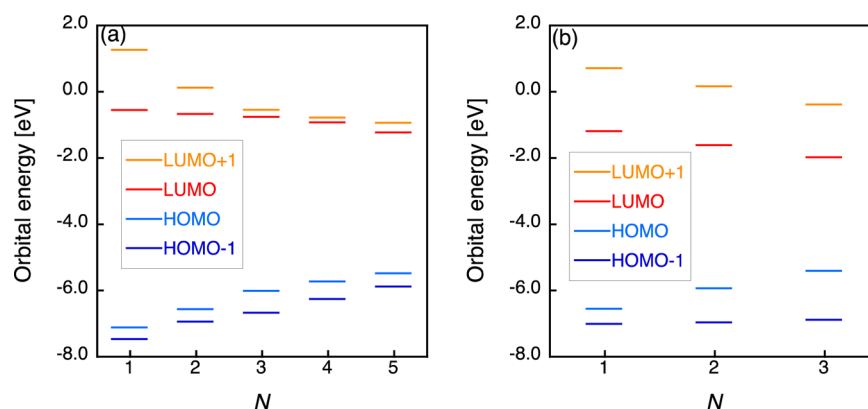
**Figure 3.** Odd electron densities,  $D_{y_i}^{\text{odd}}(\mathbf{r})$  ( $i = 0, 1$ ) and  $D_{y_0}^{\text{odd}}(\mathbf{r}) + D_{y_1}^{\text{odd}}(\mathbf{r})$ , of  $1(4)$  (a–c) and  $2(2)$  (d–f) calculated using the PUGH/6-31G\* method. The yellow surfaces represent the odd electron densities with the iso-surfaces with 0.002 au except for (e) with 0.0005 au.

$D_{y_0}^{\text{odd}}(\mathbf{r}) + D_{y_1}^{\text{odd}}(\mathbf{r})$  of  $1(4)$  and  $2(2)$  (see Scheme 1), which exhibit different relative amplitudes of  $y_0$  and  $y_1$ : ( $y_0, y_1$ ) = (0.363, 0.220) ( $y_0 \sim y_1$ , tetraradical) for  $1(4)$  and (0.491, 0.027) ( $y_0 \gg y_1$ , diradical) for  $2(2)$ . It is found for  $1(4)$  that both  $D_{y_0}^{\text{odd}}(\mathbf{r})$  and  $D_{y_1}^{\text{odd}}(\mathbf{r})$ , which are primarily distributed on the zigzag edges of both-side tetracene regions, contribute to total odd electron densities with similar amplitudes, though  $D_{y_1}^{\text{odd}}(\mathbf{r})$  exhibits more significant distributions on the zigzag edges of middle two fused rings in the both-side tetracene regions as well as slight distributions on the outer and inner six-membered rings. In contrast, for  $2(2)$ , dominant odd electron density distribution is found to come from  $D_{y_0}^{\text{odd}}(\mathbf{r})$ , which is primarily distributed on the zigzag edges of five-membered rings as well as of middle benzene rings, while  $D_{y_1}^{\text{odd}}(\mathbf{r})$  is negligible. These features turn out to exemplify the relative amplitudes of  $y_0$  and  $y_1$  and to reflect the radical sites in their resonance structures (see Figure 1). Next, we investigate the size dependence of the diradical characters of these systems. It is found from Figure 2 that with increasing  $N$ , for  $1(N)$  except for  $N = 1$  and 2, both  $y_0$  and  $y_1$  increase with similar amplitudes, while for  $2(N)$  only  $y_0$  increases with keeping  $y_1 < 0.1$ . This difference originates in their structural difference, i.e., both-side polyacenes in  $1(N)$  vs middle dicyclopenta-fused acene in  $2(N)$ , explained in Section 3.1 (see Figure 1). The slight decrease of  $y_0$  value as going from  $N = 1$  to 2 for  $1(N)$  is understood by the fact that the small diradical character originating from the central pentalene structure is weakened by attaching naphthalenes ( $N = 2$ ) with a large closed-shell nature on both sides of pentalene. As a result,  $1(N)$  ( $N \geq 2$ ) and  $2(N)$  ( $N = 1–3$ ) are found to belong to group (III) (tetraradical) and (II) (diradical), respectively.

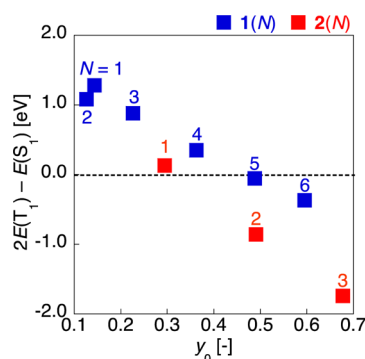
The low-lying excited states for these systems are found to be, in most cases, described well by single excitation between the HOMO-1, HOMO, LUMO, and LUMO+1 (see Table 16S in the Supporting Information for configuration), which are the frontier orbitals related to diradical characters  $y_0$  and  $y_1$  through their orbital energy gaps (see Figure 4). From the comparison between Figures 2 and 4, it is found that with increasing  $N$  both the HOMO–LUMO and HOMO-1–LUMO+1 gaps decrease and come close to each other for  $1(N)$  (in particular  $N \geq 2$ ), while the HOMO–LUMO gap decreases more significantly than the HOMO-1 – LUMO+1 gap for  $2(N)$  ( $N \leq 3$ ). These features correspond to the simultaneous increase of  $y_0$  and  $y_1$  for  $1(N)$  and to the increase of only  $y_0$  (with keeping  $y_1$  small) for  $2(N)$ .

**4.2. Relationship between Feasibility Conditions of Singlet Fission and Diradical Characters.** First, we examine the singlet fission (SF) feasibility condition (i)  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$ . Figure 5 shows  $2E(T_1) - E(S_1)$  of  $1(N)$  and  $2(N)$  for the  $y_0$  value. With increasing  $y_0$ , which is caused by increasing the fused-ring number  $N$  except for  $N = 1$  of  $1(N)$ ,  $2E(T_1) - E(S_1)$  is found to decrease almost linearly with the increase in  $y_0$  for both systems; i.e.,  $y_0 \sim 0.4$  gives  $2E(T_1) - E(S_1) \sim 0$ . Molecules  $1(N)$  with  $N = 4–6$  and  $2(N)$  with  $N = 1–3$  turn out to satisfy the feasibility condition (i) though  $2(3)$  has a large energy loss. It is thus found that the present molecules with  $y_0 > 0.2$  satisfy condition (i), while larger  $y_0$  ( $> 0.6$ ) exhibits a large energy loss.

We next investigate another SF condition (ii)  $2E(T_1) - E(T_2) < 0$ . Figure 6a shows  $2E(T_1) - E(T_2)$  of both molecules for  $y_1/y_0$ , which represents the degree of tetraradical character



**Figure 4.** Size dependences of orbital energies of the HOMO-1, HOMO, LUMO, and LUMO+1 of 1(*N*) (a) and of 2(*N*) (b).



**Figure 5.**  $y_0$  dependence of  $2E(T_1) - E(S_1)$  for 1(*N*) and 2(*N*). The number near each mark indicates *N* value. The region below the horizontal dashed line satisfies the SF condition (i)  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$ .

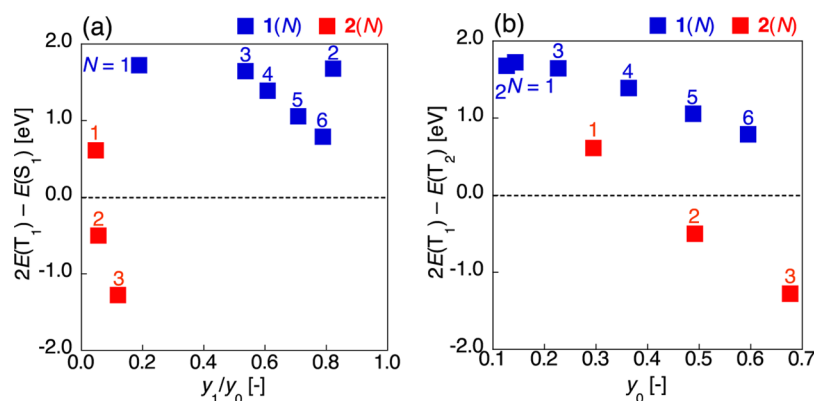
of molecules:  $y_1/y_0 \sim 1$  and  $\sim 0$  represent genuine tetraradical and diradical, respectively. Apparently, 1(*N*), which exhibits large tetraradical character except for 1(1) as discussed in Section 4.1, gives positive  $2E(T_1) - E(T_2)$ ; i.e., 1(*N*) does not satisfy condition (ii), while for 2(*N*), which exhibits almost only diradical character, 2(2) and 2(3) satisfy condition (ii). Figure 6b shows the  $y_0$  dependence of  $2E(T_1) - E(T_2)$  for 1(*N*) and 2(*N*). It is found from the configuration analysis within the TDA/TDDFT scheme that  $T_1$  is described by the HOMO  $\rightarrow$  LUMO excitation, while  $T_2$  is done by the HOMO-1  $\rightarrow$  LUMO and/or the HOMO  $\rightarrow$  LUMO+1 (see Table 10S in the

Supporting Information). From this result and the relationship between the orbital energy gaps (Figure 4) and diradical characters (Figure 2), it is predicted that with increasing *N*, for 1(*N*),  $E(T_2)$  decreases as well as  $E(T_1)$  due to the increase in  $y_0 \sim y_1$ , while for 2(*N*),  $E(T_1)$  decreases more rapidly than  $E(T_2)$  due to the increase in  $y_0$  with keeping  $y_1$  small. This feature supports the fact that 2(*N*) satisfies  $2E(T_1) - E(T_2) < 0$  for large *N* ( $\geq 2$ ), while 1(*N*) does not for  $N = 1-6$ .

In summary, 2(2) and 2(3) satisfy  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$  and  $2E(T_1) - E(T_2) < 0$  though 2(3) has a large energy loss in SF, while 1(5) and 2(1) satisfy  $2E(T_1) - E(S_1) \sim 0$  but not  $2E(T_1) - E(T_2) < 0$ . Such energy level matching conditions using the TDA/TDDFT excitation energies for 1(*N*) and 2(*N*) are found to be in agreement with the prediction by the design guideline based on the diradical characters  $y_0$  and  $y_1$ ; e.g.,  $(y_0, y_1) = (0.49, 0.03)$  for 2(2) and  $(0.68, 0.08)$  for 2(3) belong to the region with intermediate diradical without a significant tetraradical.<sup>17</sup> It is thus concluded that 2(2) and 2(3) are possible candidates for efficient SF [though 2(2) is better than 2(3) in terms of the low-energy loss] among the present systems from the viewpoint of the diradical character (or energy level matching) based design guideline.

## 5. CONCLUDING REMARKS

We have investigated the correlation between molecular structure, diradical characters, and SF feasibility conditions [(i)  $2E(T_1) - E(S_1) \sim 0$  or  $\leq 0$  and (ii)  $2E(T_1) - E(T_2) < 0$ ] from vertical excitation energies in monomers for two types of  $4n\pi$  condensed-ring systems, 1(*N*) and 2(*N*), using the tuned



**Figure 6.**  $y_1/y_0$  (a) and  $y_0$  (b) dependences of  $2E(T_1) - E(T_2)$  for 1(*N*) and 2(*N*). The regions below the horizontal dashed lines satisfy SF condition (ii)  $2E(T_1) - E(T_2) < 0$ . See legend of Figure 5 for details.

LC-RBLYP TDDFT method with the Tamm–Dancoff approximation. It turns out that the  $y_0$  and  $y_1$  values and their size dependences for these systems are different from each other and that their tendencies are understood well by their odd electron density distributions and resonance structures. The present results show that  $2(N)$  with intermediate  $y_0$  and slight  $y_1$ , which is realized in the case of  $N = 2$  and 3, satisfy both conditions (i) and (ii), while  $1(N)$  does not, in particular, (ii), for all  $N$  values examined because  $y_0$  and  $y_1$  simultaneously increase with the increase in  $N$  ( $\geq 2$ ).  $2(2)$  will be a better candidate than  $2(3)$  from the viewpoint of low energy loss if that can be prepared and takes suitable intermolecular configurations for SF as dimers, aggregates, or crystals. The relationship between the SF feasibility conditions on energy level matching and diradical characters is found to be in agreement with our previous results. The structural dependences of diradical characters,  $y_0$  and  $y_1$ , turn out to be explained by the variation in the HOMO–LUMO and HOMO–1–LUMO+1 gaps with the increase in  $N$ , respectively, which are qualitatively understood by the resonance structures for  $1(N)$  and  $2(N)$ . In conclusion, efficient singlet fission is expected for relatively small-size antiaromatic condensed-ring molecules with  $y_0 \sim 0.4$  and  $y_1/y_0 < 0.2$ , i.e., intermediate diradical character without significant tetraradical character. Toward realization of more suitable SF molecules from the viewpoint of energy efficiency, such condensed-ring molecules are expected to provide a good starting point since several chemical modifications, e.g., changing the condensed-ring structures, the introduction of hetero atoms or donor/acceptor substituents, etc., are known to adjust the diradical characters.<sup>25a,45</sup>

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Cartesian coordinates of geometries of  $1(N)$  and  $2(N)$  optimized by the UB3LYP/6-311G\* method. Influence of the optimized geometries for  $2(N)$  on the energy level matching conditions. Comparison of the excitation energies for  $1(N)$  and  $2(N)$  calculated using the TDDFT with and without the Tamm–Dancoff (TDA) approximation. Oscillator strengths of singlet excited states for  $1(N)$  and  $2(N)$ . Single excitation configurations of excited states  $S_1$ ,  $T_1$ , and  $T_2$  of  $1(N)$  and  $2(N)$  at the TDA/TDDFT tuned LC-RBLYP level of approximation. 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.

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