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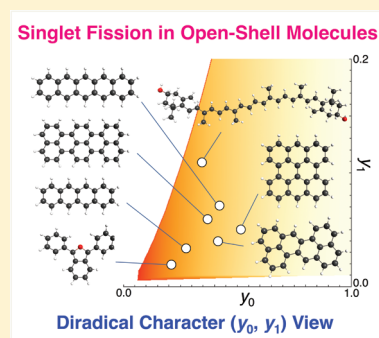
## Diradical Character View of Singlet Fission

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## Supporting Information

**ABSTRACT:** The feasibility conditions of singlet fission on the excitation energy differences are revealed as functions of the multiple diradical characters  $y_i$  [defined by the occupation numbers of the LUNO (= Lowest Unoccupied Natural Orbital) +  $i$  ( $i = 0, 1, \dots$ ), where  $0 \leq y_i \leq 1$  and  $y_i \geq y_j$  ( $i > j$ )] using the linear  $H_4$  full configuration interaction model. The diradical characters suited for singlet fission are found to lie in the region with  $y_0 > 0.10$  except for  $y_0 \sim y_1$ , though its energy efficiency is better in case of smaller  $y_0$ , to which diradical and multiradical compounds with low/intermediate diradical characters such as open-shell singlet polycyclic aromatic hydrocarbons belong. These findings indicate that the multiple diradical character is an effective indicator for exploring molecular systems for efficient singlet fission.

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

Singlet fission is one of the internal conversion processes in which a singlet exciton splits into two triplet excitons.<sup>1–3</sup> Recently, singlet fission has attracted much attention from many researchers in a broad field of chemistry and physics due to its possibility to overcome the limit of the photoelectric conversion efficiency of conventional organic photovoltaic cells (OPVs).<sup>4–6</sup> By resorting to singlet fission, the charge generation yield is theoretically expected to be improved up to 200% because two free carriers could be generated from one photon via two split triplet excitons. As a result, it has been estimated that the theoretical limit of photoelectric conversion efficiency achieves nearly 46%, whereas the conventional one does only ~34% in single gap photovoltaic cells.<sup>7</sup> However, at the moment, only a small number of molecules suited for singlet fission have been found though there have been pioneering studies by Michl et al.,<sup>3</sup> where the feasibility conditions of singlet fission have been presented on the energy level matching between the lowest singlet and triplet excited states. The most important condition of them states that twice the triplet excitation energy should be less than or nearly equal to the lowest singlet excitation energies [ $2E(T_1) \sim E(S_1)$  or  $2E(T_1) < E(S_1)$ ]. This is necessary at least for an efficient split of a singlet exciton into two triplet excitons, while most of the small organic singlet molecules turn out not to satisfy this condition due to their higher triplet excitation energy. On this point, Michl et al. have predicted that large alternant hydrocarbons are promising candidates for singlet fission due to their relatively small triplet excitation energies.<sup>4</sup> Indeed, since several large alternant hydrocarbons such as pentacene have been predicted to be classified into the open-shell singlet systems,<sup>8</sup> they have especially pointed out the importance of biradicaloids for singlet fission. However, the quantitative discussion on the relationship between open-shell character and

singlet fission has not been performed yet due to the difficulty in theoretical description and experimental measurement of the excited states for such large size open-shell molecular systems as well as in experimental estimation of the open-shell character. The purpose of this Letter is, therefore, to reveal the relationship between open-shell character and excited states contributing to singlet fission and to clarify the feasibility conditions of singlet fission as functions of open-shell character. Here, we have focused on the energetic aspect of the feasibility condition in the first step though the kinetic aspect, i.e., transition rate of singlet fission, which is affected by intermolecular electronic coupling, is also important in evaluating the efficiency of singlet fission.<sup>3,9,10</sup> To obtain a quantitative description of the open-shell character, we have employed the multiple diradical character  $y_i$ , defined by the occupation number of the lowest unoccupied natural orbital (LUNO) +  $i$  ( $i = 0, 1, \dots$ ), where  $0 \leq y_i \leq 1$  and  $y_i \geq y_j$  ( $i > j$ ).<sup>11,12</sup> For example,  $y_0$  and  $y_1$  correspond to the occupation numbers of LUNO and LUNO + 1, respectively (see Figure 1S in Supporting Information). The values of  $y_i$  reflect the bond character in the ground state; e.g., the limits of  $(y_0, y_1) = (0, 0)$ ,  $(1, 0)$ , and  $(1, 1)$  correspond to the closed shell, pure diradical, and pure tetraradical characters in the ground-state wavefunctions, respectively. It is noted that the diradical characters not only represent a bond character in the ground state but also correlate with the excited state wavefunctions and thus with excitation energies and transition properties. For instance, as shown in our previous study based on the valence configuration interaction (VCI) scheme using a simple two-site system  $A^\bullet - B^\bullet$

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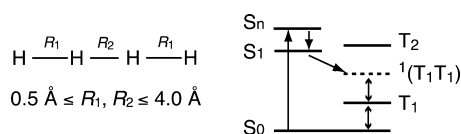
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with two electrons in two active orbitals,<sup>13</sup> the analytical form of diradical character  $y_0$  is expressed by two singlet and one triplet excitation energies.<sup>14</sup> Indeed, the diradical characters  $y_0$  based on the experimental data have shown to strongly correlate with the theoretical values.<sup>15</sup> This suggests that the diradical character ( $y_0$ ) is expected as an effective indicator of the relative excitation energies of arbitrary diradical molecular species. Indeed, such a two-site two-electron model is useful for analyzing the properties such as hyperpolarizabilities<sup>14,16</sup> and two-photon absorption cross section<sup>17,18</sup> of diradical compounds, whereas this is still insufficient for describing singlet fission. A four-electron system is found to be required at least to understand the singlet fission from the low-lying dark excited state described by doubly excited configurations, which is interpreted as a triplet–triplet coupled excited state as is well-known in long polyenes.<sup>19</sup> This suggests that singlet fission correlates with multiple diadical characters, e.g.,  $y_0$  and  $y_1$  for tetraradical systems. In this Letter, therefore, we have investigated the symmetric linear  $H_4$  model as a minimal model to clarify the relationship between the multiple diradical character ( $y_0$  and  $y_1$ ) and singlet fission. In particular, we present a viewpoint of multiple diradical characters for the feasibility conditions of singlet fission on the excitation energies proposed by Michl et al.<sup>3</sup> Such a viewpoint gives a deeper insight into the structure–property relationship in singlet fission, which is useful for understanding the mechanism and for designing molecules exhibiting highly efficient singlet fission. Indeed, the multiple diradical characters can be easily obtained by the calculation of the ground state using the broken symmetry single determinant method such as the spin-unrestricted Hartree–Fock (UHF) and density functional theory (UDFT) methods and are closely related to the bond character, chemical structures, and conventional chemical concepts like aromaticity in the ground state,<sup>20</sup> the feature of which enables us to construct practical chemical design guidelines for singlet fission.

Figure 1 shows the structure of the symmetric linear  $H_4$  model as well as the schematic diagram of excited states

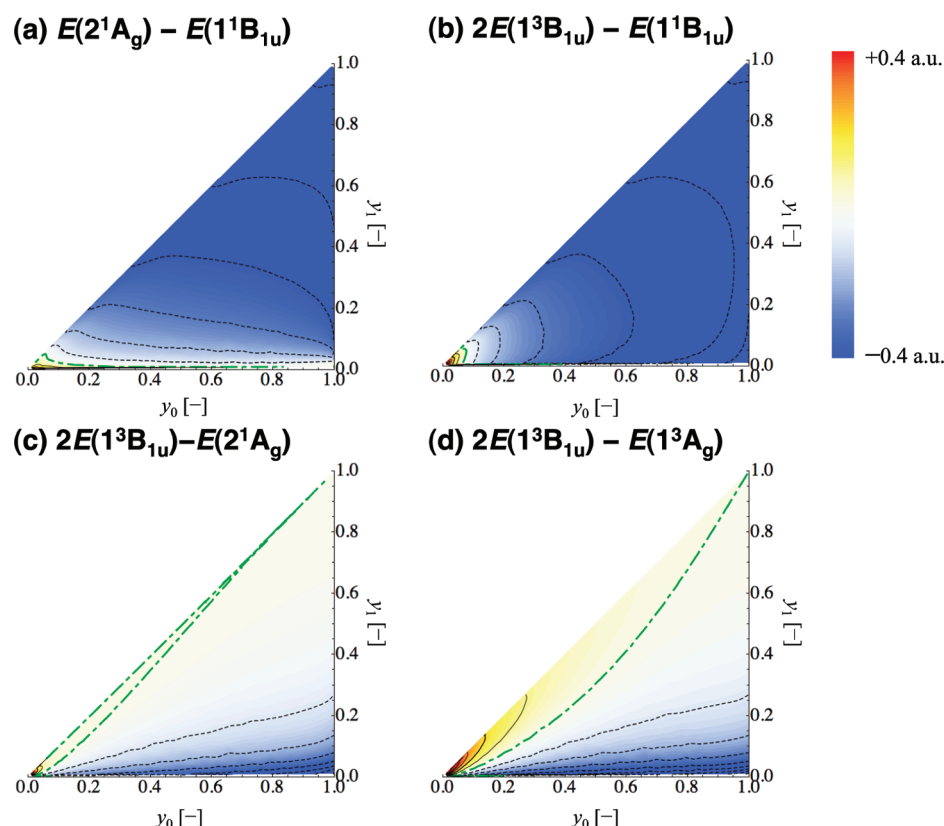


**Figure 1.** Schematic diagrams of the symmetric linear  $H_4$  model as well as of the energy states related to singlet fission.  $S_i$  and  $T_j$  represent the  $i$ th singlet and  $j$ th triplet excited states ( $i, j \geq 1$ ), respectively, while  $S_0$  represents the singlet ground state, which is taken as the energy reference (0). So,  $E(S_i)$  and  $E(T_j)$  represent the  $i$ th singlet and  $j$ th triplet excitation energies, respectively.

considered in this study, where  $S_1$ ,  $T_1$ , and  $T_2$  represent the lowest singlet, the lowest triplet, and the second lowest triplet excited states, respectively. The multiple diradical characters and excitation energies of the linear  $H_4$  model were calculated using the full configuration interaction (full CI)/STO-3G method with the GAMESS program package.<sup>21</sup> The full CI method enables us to obtain the exact results for the model, which fully include static and dynamic electron correlations. Such a model was found to give a qualitative structure–property relationship in hyperpolarizabilities described by excitation energies and transition properties of open-shell singlet systems with a wide range of open-shell characters.<sup>22,23</sup>

The interatomic distances  $R_1$  and  $R_2$  are varied from 0.5 to 4.0 Å to span a whole range of multiple diradical characters ( $0.0 < y_0, y_1 < 1.0$ ). For example, the closed shell, pure diradical, and pure tetraradical regions of  $(y_0, y_1) \sim (0, 0)$ ,  $(1, 0)$ , and  $(1, 1)$ , respectively, are found to be realized by  $(R_1, R_2)$  [Å]  $\sim (0.5, 0.5)$ ,  $(4.0, 0.5)$ , and  $(4.0, 4.0)$ , respectively. Since we have focused here on the simplified linear  $H_4$  systems modeled after monomer chromophores with a wide range of open-shell characters, the excitation energy of  $^1(T_1T_1)$ , which is the intermolecular triplet–coupled state with a singlet spin multiplicity postulated as an intermediate state on singlet fission, is approximated by twice the triplet excitation energy of an isolated molecule [ $E(^1(T_1T_1)) \sim 2E(T_1)$ ]. This approximation will be valid when the intermolecular interaction is small as in the case of molecular crystal and molecular aggregates. Under this approximation, the feasibility conditions of singlet fission are expressed as (i)  $2E(T_1) \sim E(S_1)$  or  $2E(T_1) < E(S_1)$  and (ii)  $2E(T_1) < E(T_2)$ ; the former is required to split a singlet exciton into two triplet excitons, and the latter is needed to prevent triplet exciton refusion.<sup>3,4</sup> It is noted here that efficient singlet fission is expected when  $2E(T_1)$  is close to  $E(S_1)$ , i.e., by excluding slow singlet fission in the case of a large difference between  $E(S_1)$  and  $2E(T_1)$ , and also might proceed even when  $2E(T_1) > E(S_1)$ , which is supported by a thermal activation as observed in the tetracene single crystal.<sup>24</sup> So, we rewrite the feasibility condition (i) as  $2E(T_1) \leq E(S_1)$  for simplicity. In the present model, the  $1^1B_{1u}$  and  $2^1A_g$  states could be a candidate for the lowest singlet excited state  $S_1$ , while the first and second triplet excited states ( $T_1$  and  $T_2$ ) are uniquely identified as  $1^3B_{1u}$  and  $1^3A_g$ , respectively. Thus, the four excited states,  $1^1B_{1u}$ ,  $2^1A_g$ ,  $1^3B_{1u}$ , and  $1^3A_g$ , are examined in this study.

Figure 2 shows the excitation energy differences on the  $y_0$ – $y_1$  plane,  $E(2^1A_g) - E(1^1B_{1u})$  (a),  $2E(1^3B_{1u}) - E(1^1B_{1u})$  (b),  $2E(1^3B_{1u}) - E(2^1A_g)$  (c), and  $2E(1^3B_{1u}) - E(1^3A_g)$  (d). We examine the multiple diradical character ( $y_0, y_1$ ) dependences of these energy differences to relate the feasibility conditions of singlet fission to  $y_0$  and  $y_1$ . The detailed discussion on the excitation energy and the excited configuration of each excited state is provided in the Supporting Information (see Figures 2S and 3S and Tables 1S–3S). Figure 2a shows the energy difference between the  $1^1B_{1u}$  and  $2^1A_g$  states, which characterizes the initial state of singlet fission. It is noted that, according to the classification by Michl et al.,<sup>3</sup>  $S_1 = 1^1B_{1u}$  and  $2^1A_g$  correspond to classes I and III + II, respectively, because the former primary consists of the HOMO  $\rightarrow$  LUMO singly excited configuration, while the latter consists of the HOMO  $\rightarrow$  LUMO doubly excited configuration (class III) as well as the HOMO  $-1 \rightarrow$  LUMO singly excited configuration (class II), those weights of which depend on the multiple diradical characters (see Tables 1S–3S in the Supporting Information). Note here that since both the HOMO  $\rightarrow$  LUMO doubly excited configuration and the HOMO  $-1 \rightarrow$  LUMO singly excited configuration are involved in the  $2^1A_g$  state in most systems, class III is redefined to include class II in this study. As shown in Figure 2a,  $E(2^1A_g) - E(1^1B_{1u})$  decreases with increasing  $y_1$ ; thus, the first singlet excited state  $S_1$  is characterized as the  $2^1A_g$  for larger  $y_1$ , whereas  $S_1$  is characterized as the  $1^1B_{1u}$  around  $y_1 \sim 0$  with small  $y_0$ . It implies that the initial state of singlet fission almost depends on the  $y_1$  value. This originates from the tetraradical character of the  $2^1A_g$  state, which becomes more significant when increasing the  $y_1$  value. It is found that the ionic character in the  $2^1A_g$  state decreases with increasing  $y_1$  since in that case the weight of



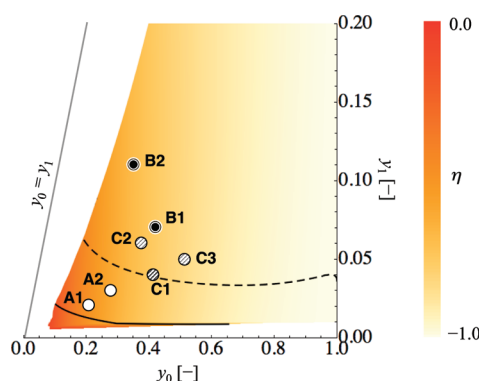
**Figure 2.** Multiple diradical character ( $y_0, y_1$ ) dependences of excitation energy differences:  $E(2^1A_g) - E(1^1B_{1u})$  (a),  $2E(1^3B_{1u}) - E(1^1B_{1u})$  (b),  $2E(1^3B_{1u}) - E(2^1A_g)$  (c), and  $2E(1^3B_{1u}) - E(1^3A_g)$  (d). The solid and dotted lines represent the contours with an interval of 0.1 a.u. for  $\Delta E > 0$  and  $\Delta E < 0$ , respectively. The bold dashed-dotted line represents the contour with  $\Delta E = 0$ .

several doubly excited configurations including the (HOMO  $\rightarrow$  LUMO) transition increases and thus the  $2^1A_g$  finally becomes a pure tetraradical state at  $(y_0, y_1) \sim (1, 1)$ . This is also confirmed by the fact that the  $2^1A_g$  state is degenerate with the ground state at  $(y_0, y_1) \sim (1, 1)$ . Such a feature is known to be realized in long polyenes and polyacenes, where the doubly excited state (composed of the triplet–triplet coupled tetraradical state) becomes lower than the singly excited state.<sup>19,25</sup> Figure 2b shows the excitation energy difference,  $2E(1^3B_{1u}) - E(1^1B_{1u})$ , the negative value of which represents one of the feasibility conditions of singlet fission [ $2E(T_1) \leq E(S_1)$ ]. We found that this feasibility condition is satisfied except for the closed-shell region  $(y_0, y_1) \sim (0, 0)$  because  $2E(1^3B_{1u}) - E(1^1B_{1u})$  rapidly decreases and becomes negative in sign when increasing  $y_0$ . This behavior is attributed to the difference in the bond characters among the ground, the lowest triplet, and the singlet excited  $1^1B_{1u}$  states. As  $y_0$  increases, that is, the diradical character in the ground state, the  $E(1^3B_{1u})$  decreases and finally becomes zero at the pure diradical limit  $(y_0, y_1) \sim (1, 0)$  because the lowest triplet state is an innate diradical wavefunction, whereas the singlet excited state  $1^1B_{1u}$  remains to be dominated by an ionic component, so that it is higher lying than the lowest triplet state. On the other hand, this behavior suggests that the energy efficiency in a conversion of singlet exciton into two triplet excitons tends to become worse with increasing  $y_0$ . Figure 2c shows the excitation energy difference,  $2E(1^3B_{1u}) - E(2^1A_g)$ , the negative value of which also represents one of the feasibility conditions of singlet fission [ $2E(T_1) \leq E(S_1)$ ]. Interestingly,  $E(2^1A_g) \sim 2E(1^3B_{1u})$  is satisfied in a wide range of  $y_0$  for  $y_1 > 0.2$  because the  $2^1A_g$

could be regarded as an intramolecular triplet–triplet coupled excited state in the case of large  $y_1$ . On the other hand,  $E(2^1A_g) \sim 2E(1^3B_{1u})$  is not satisfied around  $y_0 \sim 0$  because the  $2^1A_g$  is no longer the triplet–triplet coupled wavefunction due to the large amount of the ionic contributions of the (HOMO  $- 1 \rightarrow$  LUMO) singly excited configuration in the  $2^1A_g$  in that  $y_0$  region. Figure 2d shows the excitation energy difference,  $2E(1^3B_{1u}) - E(2^3A_g)$ , the negative value of which satisfies the feasibility condition [ $2E(T_1) < E(T_2)$ ]. It is noted that this condition is required independent of the character of  $S_1$ . This condition is found to be satisfied except for  $y_0 \sim 0$  and  $y_0 \sim y_1$  regions, which implies that singlet fission would be suppressed in the case of molecules with nearly closed-shell or high tetraradical character.

Figure 3 illustrates the region satisfying the feasibility conditions  $2E(T_1) \leq E(S_1)$  and  $2E(T_1) \leq E(T_2)$  on the  $y_0$ – $y_1$  plane together with the density plot of  $\eta = [2E(1^3B_{1u}) - E(1^1B_{1u})]/E(1^1B_{1u})$ , where the darker density region exhibits the region with higher energy efficiency ( $\sim 0$  for the highest efficiency) of singlet fission from the  $1^1B_{1u}$  state after absorption of light. The auxiliary lines,  $[E(2^1A_g) - E(1^1B_{1u})]/E(1^1B_{1u}) = 0$  (solid) and  $-0.3$  (dashed), are also shown to characterize the relative energy level of  $1^1B_{1u}$  and  $2^1A_g$ . It is found that the feasibility condition of singlet fission lies in the open-shell region ( $y_0 > 0.1$  in the present case) except for the highly tetraradical region ( $y_0 \sim y_1$ ), whereas the energy efficiency of singlet fission gets worse with increasing  $y_0$  due to an excessive decrease in the triplet excitation energy  $E(T_1)$ . It is also noted that the doubly excited state  $2^1A_g$  tends to be the lowest singlet excited state  $S_1$  instead of the singly





**Figure 3.** Feasibility region of singlet fission on the  $y_0$ – $y_1$  plane using the linear  $H_4$  model. The density plot represents the energy efficiency with a function of  $\eta = [2E(1^3B_{1u}) - E(1^1B_{1u})]/E(1^1B_{1u})$ , where the darker region has higher efficiency. The solid and dashed lines show  $[E(2^1A_g) - E(1^1B_{1u})]/E(1^1B_{1u}) = 0$  and  $-0.3$ , respectively, which indicates the relative energy level between  $2^1A_g$  and  $1^1B_{1u}$ . Symbols A1, A2, B1, B2, C1, C2, and C3 represent the multiple diradical characters of tetracene, 1,3-diphenylisobenzofuran, pentacene, zeaxanthin, zethrene, PAH[2,5] and PAH[3,3], respectively (see Table 1), calculated using the PUHF/6-31G\* level of approximation (see Supporting Information).<sup>11,12,38</sup>

excited state  $1^1B_{1u}$  in the higher  $y_1$  region; that is, class III molecule is predicted to be characterized by the higher multiradical nature than class I. To assess the reliability of these results, we have examined the multiple diradical characters for several  $\pi$ -conjugated molecules (Table 1) [see

**Table 1. Multiple Diradical Characters ( $y_0$ ,  $y_1$ )<sup>a</sup> and Primary Excited Configurations in the Lowest Singlet Excited States ( $S_1$ ) of Several Real  $\pi$ -Conjugated Molecules**

molecule	$y_0$	$y_1$	primary configuration in $S_1$
tetracene <sup>b</sup>	0.28	0.03	singly excited <sup>d</sup>
1,3-diphenylisobenzofuran <sup>b</sup>	0.21	0.02	singly excited <sup>e</sup>
pentacene <sup>b</sup>	0.42	0.07	doubly excited <sup>f</sup>
zeaxanthin <sup>b</sup>	0.35	0.11	doubly excited <sup>g</sup>
zethrene <sup>b</sup>	0.41	0.04	–
PAH[2,5] <sup>c</sup>	0.37	0.06	–
PAH[3,3] <sup>c</sup>	0.51	0.05	–

<sup>a</sup>Obtained from PUHF/6-31G\* calculations (see Supporting Information). <sup>b</sup>Geometries are optimized by the RB3LYP/6-311G\* level of theory. <sup>c</sup>Ref 35. <sup>d</sup>Ref 30. <sup>e</sup>Ref 31. <sup>f</sup>Ref 25. <sup>g</sup>Ref 29.

Supporting Information for their structures (Figure 4S), calculation method of  $y_0$  and  $y_1$ , and experimental excited states (Table 4S)]. Indeed, tetracene (A1),<sup>1,2</sup> 1,3-diphenylisobenzofuran (A2),<sup>26</sup> pentacene (B1),<sup>27</sup> and zeaxanthin (B2),<sup>28</sup> for which efficient singlet fissions were experimentally observed, are found to lie in the region with  $y_0 > 0.2$ , which indicates that they have open-shell character in the ground state. In addition, pentacene (B1) and zeaxanthin (B2), which are predicted to have doubly excited character in the  $S_1$  state,<sup>25,29</sup> exhibit a higher  $y_1$  value than tetracene (A1) and 1,3-diphenylisobenzofuran (A2), which are predicted to have singly excited character in  $S_1$ <sup>30,31</sup> though they lie slightly outside the region with  $E(2^1A_g) - E(1^1B_{1u}) \geq 0$  in the present model. Nevertheless, the relative features of singlet fission between (A1, A2) and (B1, B2), which would be classified as classes I and III, respectively, are clearly distinguished on the  $y_0$ – $y_1$  plane. These results indicate that the multiple diradical

character is useful for semiquantitative description of the feasibility conditions of singlet fission, though it is still difficult to predict precise thresholds of multiple diradical characters for efficient singlet fission due to the limitation of the minimum  $H_4$  model and/or to the approximate calculation of diradical character. Finally, it is noteworthy that three polycyclic aromatic hydrocarbons, i.e., zethrene (C1), PAH[2,5] (C2), and PAH[3,3] (C3) (where PAHs[X,Y] indicate the rectangular graphenes, where X and Y denote the number of fused benzene rings in the zigzag and armchair edges, respectively), which have recently attracted a great deal of attention due to their open-shell singlet ground states<sup>32,33</sup> and are classified into delocalized multiradical systems,<sup>34,35</sup> lie in the feasibility region of singlet fission (see Table 1 and Figure 3) though they have not been examined from the viewpoint of singlet fission. As seen from Figure 3, these PAHs are predicted to lie in the boundary region between classes I and III due to their relatively large  $y_0$  and non-negligible  $y_1$  values. Also, judging from the increased behavior of  $y_0$  and  $y_1$  depending on the size of PAHs,<sup>35</sup> several large-size PAHs are expected to exhibit efficient singlet fission as class III molecules. To verify this prediction, we need to perform strongly electron-correlated calculations of the low-lying excited states in large size PAHs using the multireference perturbation (MRMP), coupled cluster (MRCC), and spin-flip time-dependent DFT methods,<sup>36,37</sup> which are also challenging themes in quantum chemistry.

In summary, we have proposed a novel viewpoint of multiple diradical character for the feasibility condition of singlet fission. It has been found that the multiple diradical character is an effective indicator for exploring molecular systems for singlet fission; that is, the feasibility conditions of singlet fission are satisfied when a molecule has open-shell character ( $y_0 > 0.1$ ) except for the highly tetraradical case ( $y_0 \sim y_1$ ), though its energy efficiency is better in the case of smaller  $y_0$ . This indicates that the efficient singlet fission tends to occur in molecules in the singlet ground state with low/intermediate diradical characters rather than with complete open-shell or closed-shell ones. Indeed, the importance of the above appropriate tetraradical character, which realizes class III molecules with low singlet doubly excited state with  $A_g$  symmetry, has been highlighted in recent theoretical and experimental studies on singlet fission.<sup>10,25,39</sup> Because such intermediate open-shell singlet character is recently predicted to be realized in several PAHs<sup>32,33</sup> and other thermally stable compounds including diphenalenyl diradicaloids,<sup>40–42</sup> the present results will stimulate theoretical and experimental investigations on singlet fission in open-shell singlet molecules from the viewpoint of multiple diradical characters, which pave the way toward realizing highly efficient OPVs.

## ■ ASSOCIATED CONTENT

### § Supporting Information

The definition of the multiple diradical character. The multiple diradical character dependencies of the excitation energies and the excited configurations of the  $1^1B_{1u}$ ,  $2^1A_g$ ,  $1^3B_{1u}$ , and  $1^3A_g$  states in the linear  $H_4$  model. The molecular structures of tetracene, diphenylisobenzofuran, pentacene, zeaxanthin, zethrene, PAH[2,5], and PAH[3,3]. The calculation procedure of multiple diradical character by the PUHF method. The relationship between experimental excitation energies and calculated multiple diradical characters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ ACKNOWLEDGMENTS

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