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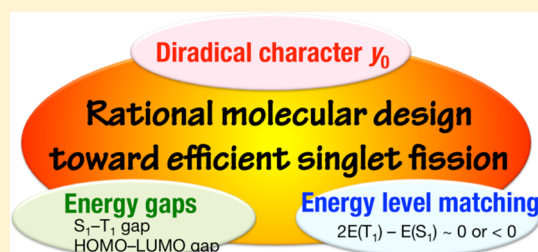
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S Supporting Information

ABSTRACT: The fundamental of diradical-character-based molecular design for singlet fission is clarified through the correlation between the diradical character, the first singlet (S_1) and triplet (T_1) excitation energies, the frontier orbital energy gap, and the energy level matching condition ($2E(T_1) - E(S_1) \approx 0$ or < 0) for singlet fission by using the analytical solution of the electronic structure for a model system with two electrons in two orbitals. Moreover, the S_1 – T_1 gap is found to be a key factor for governing the amplitude of $E(T_1)$ for $2E(T_1) - E(S_1) \approx 0$. These findings are indeed justified by the spin-flip time-dependent density functional theory calculations for a series of typical alternant/nonalternant hydrocarbons, that is, phenacenes, acenes, and isobenzofulvene. The present results demonstrate that a weak diradical character is the underlying concept for efficient singlet fission molecules.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory



Singlet fission has recently attracted many researchers due to the possibility to overcome the Shockley–Queisser efficiency limit in conventional photovoltaic systems.¹ Indeed, several types of singlet fission photovoltaic systems have been extensively explored,^{2,3} and the mechanism of singlet fission has also been intensively investigated for several acene derivatives.^{4,5} On the other hand, designing novel molecules for efficient singlet fission is less well investigated; indeed, to date, only a few number of molecules have been known to exhibit an efficient singlet fission.

The pioneering works in designing singlet fission molecules were done by Michl and co-workers, who explored singlet fission molecules by using the energy level matching conditions $2E(T_1) \approx E(S_1)$ or $2E(T_1) < E(S_1)$ for causing singlet fission and $2E(T_1) < E(T_2)$ for suppressing the recombination process of triplet excitons,⁶ where $E(S_1)$, $E(T_1)$, and $E(T_2)$ indicate the excitation energies of the first singlet (S_1), the first triplet (T_1), and the second triplet (T_2) excited states, respectively. On the basis of the first condition, that is, $2E(T_1) \approx E(S_1)$ or $2E(T_1) < E(S_1)$, they particularly predicted that “alternant hydrocarbons” or “diradicaloids” are promising candidates for singlet fission because, in general, the former has a large S_1 – T_1 gap originating in the paired spatial distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the latter is expected to possess a small S_0 – T_1 gap, where S_0 indicates the singlet ground state.⁶

Inspired by the idea of a diradicaloid, we previously introduced a quantitative index of singlet open-shell nature, multiple diradical characters (y_0, y_1),⁷ for exploring novel singlet fission molecules and predicted that the energy level matching

conditions are satisfied by a molecule with a weak/intermediate diradical character (indicated by y_0) as well as with a quite weak tetraradical character (indicated by y_1).⁸ Although our previous studies have clarified the semiquantitative correlation between y_i and the energy level matching conditions for $4n\pi$ electron systems⁹ as well as for a series of oligorylenes,¹⁰ the fundamental of the diradical-character-based molecular design guideline has not been revealed yet. In addition, the quantitative discussion on the comprehensive correlation between the molecular structure (for example, an alternant hydrocarbon and/or a diradical form in the resonance structure), the diradical character, and the energy level matching condition has also been unexplored yet. The purpose of the present study is to clarify this correlation, which gives the fundamental of the diradical-character-based molecular design for singlet fission. The present results will contribute to a realization of novel singlet fission molecules.

Here, we focus on the case that both S_1 and T_1 states are mainly described by a HOMO \rightarrow LUMO singly excited configuration and a system has a singlet ground state [$E(T_1) > 0$]. The analytical expressions of the diradical character (y_0) and the excitation energy difference concerning the first energy level matching condition [$2E(T_1) - E(S_1)$] are investigated for a two-site system with two electrons in two active orbitals by using the valence configuration interaction (VCI) method.^{11,12} The VCI method provides the exact analytical equation for the present model system by including the full-configuration

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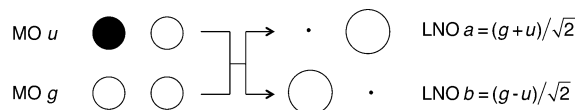
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interaction in the active space composed of the HOMO and LUMO. In this study, although the second diradical character, y_1 , and the second energy level matching condition, $2E(T_1) < E(T_2)$, are not considered due to the limitation of a two-electron system, the results based on the first condition will be useful for designing singlet fission molecules because relatively small size hydrocarbon systems with small/intermediate y_0 values, which satisfy the first condition, mostly tend to give much smaller y_1 values ($y_1 \ll y_0$), which satisfy the second condition.⁸ The validity of the results obtained for the two-site system is demonstrated for a series of phenacenes, acenes, and isobenzofulvenes by spin-flip time-dependent density functional theory (SFDFT) calculations. We also quantitatively discuss the effect of molecular structure on the diradical character and the energy level matching condition.

In the VCI scheme,¹² we consider a two-site system, $A^\bullet-B^\bullet$, with two electrons in two orbitals. Using the spatial symmetry-adapted bonding (g) and antibonding (u) MOs, the localized natural orbitals (LNOs) are defined as $a(x) = [g(x) + u(x)]/\sqrt{2}$ and $b(x) = [g(x) - u(x)]/\sqrt{2}$ (see Scheme 1). The LNOs

Scheme 1. Relationship between MOs (g and u) and LNOs (a and b) in the Two-Site Model with Two Electrons in Two Orbitals



are mainly localized on one site (A or B) with small tails on the other site and satisfy the orthogonal condition, $\langle a|b \rangle = 0$. The LNOs are interpreted as the magnetic orbitals constructed from bonding and antibonding MOs. Note that the degree of spatial overlap between MOs g and u shows a mutually opposite tendency to that between a and b ; for example, when the MOs have a larger spatial overlap on each site, the LNOs have a smaller spatial overlap (see Scheme 1).

For the two-site system, the diradical character, y_0 , which is defined as twice the doubly excited configuration in the singlet ground state,¹³ is given by¹²

$$y_0 = 1 - \frac{1}{\sqrt{1 + \left(\frac{U}{4|t_{ab}|}\right)^2}} \quad (0 \leq y_0 \leq 1) \quad (1)$$

where $U [\equiv U_{aa} - U_{ab} = (a|a|a) - (a|a|b|b)]$ is an effective Coulomb repulsion, which is the difference between an on-site Coulomb repulsion, $(a|a|a)$, and an intersite Coulomb repulsion, $(a|a|b|b)$. $t_{ab} [\equiv (a|f|b)]$ is a transfer integral, which represents the through-bond mobility of an electron between site a and b . The $y_0 = 0$ and 1 correspond to the singlet ground states with closed-shell and purely diradical wave functions, respectively, and y_0 also corresponds to the occupation number of the lowest unoccupied natural orbital in the two-site model.¹² Equation 1 indicates that a localization of electrons leads to the high y_0 value due to the large electron repulsion (U) and small mobility of the electron (t_{ab}).

In the present model, the lowest singlet [$E(S_1)$] and triplet [$E(T_1)$] excitation energies are expressed as a function of y_0 ¹⁴

$$E(S_1) = \frac{U}{2} \left(1 + \frac{1}{\sqrt{1 - (1 - y_0)^2}} \right) - 2K_{ab}$$

$$E(T_1) = \frac{U}{2} \left(-1 + \frac{1}{\sqrt{1 - (1 - y_0)^2}} \right) - 2K_{ab} \quad (2)$$

where $K_{ab} [= (a|b|a|b) \geq 0]$ is a direct exchange integral in the LNO basis. Note that y_0 intimately relates to the excitation energies. Indeed, y_0 can be estimated by using several excitation energies obtained from experiment.¹⁵

From eq 2, one easily obtains

$$U = E(S_1) - E(T_1) \quad (3)$$

One can find that U corresponds to twice the exchange interaction between bonding and antibonding MOs ($=2K_{gu}$).¹⁶ Note that this is different from K_{ab} expressed in the LNO picture). Also, as shown in the previous study,¹⁴ t_{ab} corresponds to the $g-u$ orbital energy gap averaged over α and β orbitals of the T_1 state for the two-site system

$$t_{ab} = -\frac{1}{2} \Delta \bar{\epsilon}^T \quad (4)$$

where $\Delta \bar{\epsilon}^T \equiv 1/2(\Delta \epsilon^\alpha + \Delta \epsilon^\beta)$ and $\Delta \epsilon^i$ ($i = \alpha$ and β) represents the $g-u$ orbital energy gap of the T_1 state. Equation 4 can be interpreted as a higher bonding character leads to a larger MO gap ($\Delta \bar{\epsilon}^T$) as well as a higher through-bond mobility of electrons between the LNOs (t_{ab}). Equations 1, 3, and 4 indicate that y_0 is interpreted as a quantitative indicator for the ratio between the S_1-T_1 gap (U) and the frontier orbital gap ($|t_{ab}|$). For example, an increase in the S_1-T_1 gap (U) and/or a decrease in the frontier orbital gap (t_{ab}) lead to an increase in y_0 . This agrees well with our intuitive understanding that a relatively small $E(T_1)$ and/or a small frontier orbital gap leads to a high diradical character.

From eqs 2 and 3, the dimensionless energy level matching condition in the two-site system is given by

$$f \equiv \frac{2E(T_1) - E(S_1)}{U}$$

$$= -\frac{3}{2} + \frac{1}{2\sqrt{1 - (1 - y_0)^2}} - \frac{2K_{ab}}{U}, \quad (f \geq -1) \quad (5)$$

where $f \geq -1$ is obtained by assuming a singlet ground state [$E(T_1) \geq 0$] in eq 2. Equation 5 indicates that a sufficiently large y_0 and/or $2K_{ab}/U$ (see Scheme 1) are required for satisfying the energy level matching condition ($f \approx 0$ or $f < 0$).

In real molecules, U and K_{ab} generally show mutually opposite dependences on the degree of spatial overlap between MOs; for example, when the frontier MOs g and u have mutually similar spatial distributions, one obtains a large U and small K_{ab} originating in the separated distributions between LNOs a and b (see Scheme 1). The third term of eq 5, $2K_{ab}/U$, is therefore interpreted as the index for the degree of spatial overlap between the frontier MOs. It is also noted here that y_0 and $2K_{ab}/U$ generally show a trade-off relationship due to their dependences on U ; for example, an increase in the U value tends to lead not only to an increase in the y_0 value (see eq 1) but also to a decrease in the $2K_{ab}/U$ value.

By assuming one of the energy level matching conditions ($f \approx 0$ or $f < 0$), we obtain

$$\begin{aligned}
 E(S_1) &\approx 2U & \text{and} & & E(T_1) &\approx U \\
 \text{or} \\
 E(S_1) &< 2U & \text{and} & & E(T_1) &< U
 \end{aligned}
 \quad (6)$$

Although this is the natural consequence derived from the functional forms of $U [=E(S_1) - E(T_1)]$ and the energy level matching condition $[=2E(T_1) - E(S_1) \approx 0 \text{ or } < 0]$, eq 6 provides the important understanding that U determines the maximum limit of $E(S_1)$ and $E(T_1)$ for a singlet fission molecule. A sufficiently large $E(T_1)$ would be favorable to a singlet fission photovoltaic system because $E(T_1)$ determines the driving force of the charge generation. According to the theoretical prediction for an ideal condition, the appropriate $E(T_1)$ is indeed predicted to be about 1 eV.^{1,6} In such a system, the third term of eq 5 ($2K_{ab}/U$) should be small due to the relatively large U value. As a result, y_0 is expected to be an essential factor for tuning f (eq 5) to satisfy the energy level matching condition, $f \approx 0$ or $f < 0$.

Figure 1 shows the variation of f as a function of y_0 obtained by eq 5 with $2K_{ab}/U = 0.0, 0.2, 0.4$, and 0.6 . As predicted from

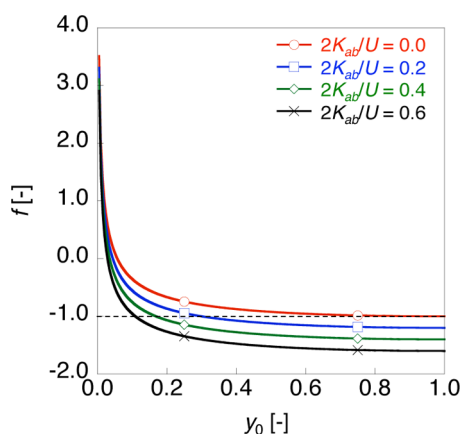
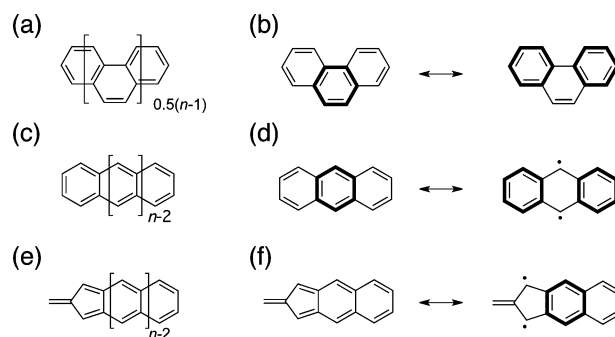


Figure 1. Variation of dimensionless $f = [2E(T_1) - E(S_1)]/U$ as a function of diradical character y_0 for the two-site system calculated using the VCI method (see eq 5). $E(T_1) > 0$ is satisfied for $f > -1$ (upper side of the black dotted line).

eq 5, f decreases with the increase in y_0 . This behavior can be interpreted as follows; an increase in a S_1 – T_1 gap (U) and/or a decrease in the frontier MO gap ($2|t_{ab}|$) lead to an increase in y_0 (see eq 1) as well as to a decrease in $f [\propto 2E(T_1) - E(S_1)]$; see eq 5] by inducing the relative decrease in $E(T_1)$ due to $E(T_1) < E(S_1)$. Therefore, the performance function of the energy level matching condition, $2E(T_1) - E(S_1)$, is found to indirectly correlate with y_0 through the ratio between the S_1 – T_1 gap (U) and frontier MO gap ($2|t_{ab}|$). In addition, it is also found that the optimal energy level matching ($f \approx 0$) is achieved for $y_0|_{f \approx 0} \approx 0.06$ at $2K_{ab}/U = 0$ and that an increase in $2K_{ab}/U$ leads to a decrease in $y_0|_{f \approx 0}$. This result indicates that molecules with weak diradical character are the best candidates for efficient singlet fission within the present model. It should be emphasized that $y_0|_{f \approx 0}$ is quite small but is not negligible due to the rapid increase in f around the region of $f \approx 0$ with the slight decrease in y_0 for $y_0 < 0.1$ (see Figure 1). Indeed, tetracene, pentacene, and relatively small size oligorylenes, which have been generally recognized as the closed-shell singlet molecules but in fact have found to show weak diradical character,^{8,10} are the candidates for singlet fission.

To confirm the validity of the above discussion on the two-site model, we investigate the three real molecules, $[n]$ -phenacenes ($[n]$ Ph, Scheme 2a), $[n]$ acenes ($[n]$ Ac, Scheme

Scheme 2. Molecular Structures of $[n]$ Pheacene (a), $[n]$ Acenes (c), and a Series of Isobenzofulvene (e), Together with Their Resonance Structures at $n = 3$ (b, d, and f), where n Indicates the Number of Fused Rings^a



^aThe benzenoid forms are highlighted by the bold lines.

2c), and a series of isobenzofulvene ($[n]$ Bf, Scheme 2e), which have mutually the same composition formula with their counterparts. U , $|t_{ab}|$, and y_0 are approximately estimated by using eqs 3, 4, and 1, respectively. Note that $[n]$ Ph and $[n]$ Ac belong to the alternant hydrocarbons, while $[n]$ Bf does not. Also, according to the Clar's sextet rule,¹⁷ in which the number of sextet (benzenoid) forms determines the stability of a system, $[n]$ Ac and $[n]$ Bf could take the diradical form in their resonance structures (see Scheme 2d and f).

Figure 2 shows the variations of U , $|t_{ab}|$, and y_0 as the functions of the number of rings, n , for $2 \leq n \leq 5$ (Figure 2a–c, respectively). Here, we summarize the characteristic features of $[n]$ Ph, $[n]$ Ac, and $[n]$ Bf, while the details of the molecular size dependence are discussed in the Supporting Information. In Figure 2a, we found that the two alternant hydrocarbons, $[n]$ Ac and $[n]$ Ph, have larger U values than the counterpart of the nonalternant hydrocarbon, $[n]$ Bf, as is well-known by the Coulson–Rushbrooke pairing theorem,¹⁸ in which an alternant hydrocarbon has a large spatial overlap between the HOMO and LUMO due to the pairing character. In Figure 2b, $[n]$ Ac and $[n]$ Bf are found to have the smaller HOMO–LUMO gaps, $|t_{ab}|$, than $[n]$ Ph due to the higher nonbonding nature in the HOMO and LUMO as confirmed by the existence of the diradical form in the resonance structure (see Scheme 2). In Figure 2c, we found relatively large y_0 values for $[n]$ Bf and $[n]$ Ac as compared to that for $[n]$ Ph. The finite y_0 values of $[n]$ Ac and $[n]$ Bf reflect the relatively small $|t_{ab}|$ values as compared to the U values (see Figure 2a and b and eq 1) and are engaged with the existence of the diradical forms in their resonance structures (see Scheme 2b, d, and f). This indicates the effectiveness of Clar's sextet theory¹⁷ for qualitative estimation of a finite diradical character of a molecule.

Figure 3 shows the variation of $f [=2E(T_1) - E(S_1)]/U$ for $[n]$ Ph, $[n]$ Ac, $[n]$ Bf, and the two-site model (see eq 5) as functions of y_0 . Here, y_0 's of the real molecules are calculated by using the S_1 – T_1 gap (U , eq 3), the frontier orbital gap ($|t_{ab}|$, eq 4), and eq 1. We found that the two-site model with $2K_{ab}/U = 0$ (black line) shows good agreement with those of the alternant hydrocarbons, $[n]$ Ph (red circle) and $[n]$ Ac (blue-colored square) for $2 \leq n \leq 5$, while $[n]$ Bf (green rhombus)

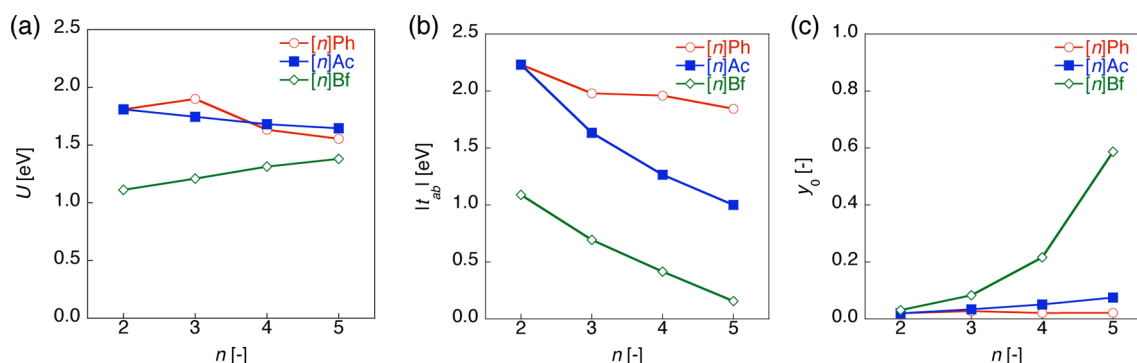


Figure 2. Variations of U (a), $|t_{ab}|$ (b), and y_0 (c) as functions of n for $[n]$ Ph, $[n]$ Ac, and $[n]$ Bf. U is evaluated by eq 3 using the SFDFD method, $|t_{ab}|$ is calculated by eq 4 using the spin-unrestricted DFT method, and y_0 is evaluated from eq 1 using U and $|t_{ab}|$.

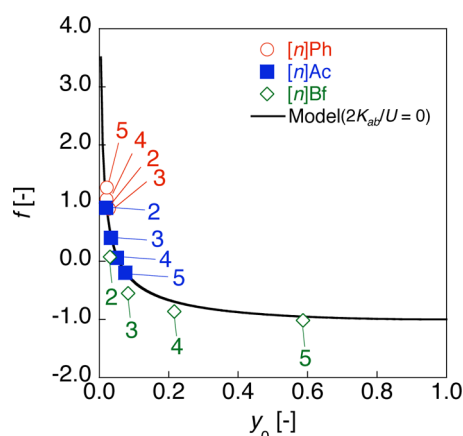


Figure 3. Variation of $f = [2E(T_1) - E(S_1)]/U$ as a function of y_0 (eq 1) for $[n]$ Ph, $[n]$ Ac, and $[n]$ Bf, as well as that for the two-site model (obtained by using eq 5 with $2K_{ab}/U = 0.0$). The inserted numbers represent n ($2 \leq n \leq 5$).

gives the slightly lower f value. This deviation in $[n]$ Bf is due to the larger $2K_{ab}/U$ of $[n]$ Bf than others, originating in the smaller spatial overlap between the HOMO and LUMO in nonalternant hydrocarbons (see Figure 1 as well as the detailed data on $2K_{ab}/U$ in the Supporting Information). It is worth noting that all $[n]$ Ph, which have quite small y_0 (~ 0.02) values, do not satisfy the energy level matching condition, $f \approx 0$ or < 0 , for $2 \leq n \leq 5$. In contrast, $[n]$ Ac ($n \geq 4$) and $[n]$ Bf ($n \geq 2$), which show sufficient y_0 values, are found to satisfy $f \approx 0$ or < 0 . This indicates the importance of the diradical form in the resonance structures, that is, the finite diradical character, whether or not a molecule belongs to alternant hydrocarbons, for satisfying the energy level matching condition.

We further investigated the amplitudes of excitation energies of $[4]$ Ac and $[2]$ Bf, both of which satisfy $f \approx 0$ (see Table 1). It is found that $E(S_1)$ and $E(T_1)$ of $[4]$ Ac (3.46 and 1.78 eV, respectively) are larger than those of $[2]$ Bf (2.31 and 1.20 eV, respectively). As expected by eq 6 and the Coulson–

Table 1. $E(S_1)$, $E(T_1)$, U , $|t_{ab}|$, y_0 , and f of $[4]$ Ac and $[2]$ Bf, Which Have $f \approx 0$

molecule	$E(S_1)^a$	$E(T_1)^a$	U^a	$ t_{ab} ^a$	y_0	f
$[4]$ Ac	3.46	1.78	1.68	1.40	0.05	0.06
$[2]$ Bf	2.31	1.20	1.11	1.09	0.03	0.08

^aIn units of eV.

Rushbrooke pairing theorem, this difference in excitation energies reflects the larger U value of $[4]$ Ac than that of $[2]$ Bf, originating in the larger spatial overlap between the HOMO and LUMO of an alternant hydrocarbon, $[4]$ Ac.⁶ This result clearly indicates the importance of U and the molecular structure for tuning the amplitudes of excitation energies of a singlet fission molecule.

In summary, we revealed a general expression for the correlation between diradical character and the energy level matching condition for singlet fission by using the valence configuration interaction scheme for a two-site model. The dimensionless $[2E(T_1) - E(S_1)]/U$ ($=f$) in the energy level matching condition for singlet fission is clarified to be correlated with the diradical character (y_0) through the ratio between the S_1 – T_1 gap (U) and the frontier orbital gap ($2|t_{ab}|$) (see eqs 1–5). Moreover, the best energy level matching ($f \approx 0$) is found to be satisfied for a quite weak but not negligible diradical character ($0.00 < y_0 \leq 0.06$) within the two-site model (see Figure 1). Importantly, this is a general result being independent from the molecular species. Therefore, we have concluded that a weak diradical character is an essential factor for a molecule exhibiting efficient singlet fission. One will confirm this result from singlet fission measurements and quantum chemical calculation of y_0 or experimental estimation of y_0 using several observed excitation energies.¹⁵ The difference in the molecular structures of $[n]$ Ph, $[n]$ Ac, and $[n]$ Bf evidenced the importance of the diradical form in the resonance structure (contributing to increasing y_0 values), whether or not a molecule belongs to alternant hydrocarbons, for satisfying the energy level matching condition (see Scheme 2 and Figures 2 and 3). The correlations among the resonance structure, diradical character, and excitation energies will be key factors for the rational design of a singlet fission molecule. In addition, we found that the amplitude of $E(T_1)$ at $f \approx 0$ is nearly equal to the S_1 – T_1 gap (U), which correlates with the spatial overlap between the HOMO and LUMO (see eq 6 and Table 1). This will open up the way to the rational tuning of $E(T_1)$, which controls the driving force of exciton dissociation in singlet fission photovoltaic systems. These results will contribute to deepening the fundamental understanding of the electronic structure of singlet fission molecules and will stimulate the investigation of the rational molecular design of novel singlet fission molecules toward realization of future photovoltaic systems.

■ ASSOCIATED CONTENT

Supporting Information

Computational details. Molecular size dependences of U and $|t_{ab}|$ shown in Figure 2. $2K_{ab}/U$ of the real molecules calculated using the complete active space configuration interaction (CASSCI) method. 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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