Supporting Information on “Diradical Character View of Singlet Fission”

Takuya Minami* and Masayoshi Nakano*

Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University,
Toyonaka, Osaka 560-8531, Japan

Contents

1. Definition of the multiple diradical character (**Figure 1S**)
2. Multiple diradical character dependences of excitation energies and excited configurations of 1^1B_{1u} , 2^1A_g , 1^3B_{1u} , and 1^3A_g states in the linear H_4 model (**Figure 2S, Figure 3S, Table 1S, Table 2S, and Table 3S**)
3. Molecular structures of tetracene, 1,3-diphenylisobenzofran, pentacene, zexanthin, zethrene, PAH[2,5], and PAH[3,3] (**Figure 4S**)
4. Calculation procedure of multiple diradical character using the PUHF method
5. Relationship between experimental excitation energies and calculated multiple diradical characters (**Table 4S**)

1. Definition of the multiple diradical character

The open-shell character can be described by the multiple diradical characters y_i , which are defined as the occupation numbers of the LUNO+ i , where $i = 0, 1, \dots$ (LUNO = Lowest Unoccupied Natural Orbital):

$$y_i = n_{\text{LUNO}+i}, \quad (\text{s1})$$

where y_i takes a value ranging from 0 to 1. The value of y_0 (occupation number of the LUNO) increases from 0 to 1, which corresponds to the increase in the mixing of the anti-bonding (LUNO) and bonding [HONO (Highest Occupied Natural Orbital)] orbitals in the singlet ground-state wavefunction. In fact, the diradical character was originally defined in the multiconfigurational self-consistent field (MC-SCF) theory as twice the weight of the doubly-excited configuration in the singlet ground state, but generally it is formally expressed by eq. s1 [1,2].

Figure 1S. Definition of multiple diradical character (y_i)

2. Multiple diradical character dependences of excitation energies of 1^1B_{1u} , 2^1A_g , 1^3B_{1u} , and 1^3A_g states in the linear H_4 model

Figure 2S represents the excitation energies of the 1^1B_{1u} (a), 2^1A_g (b), 1^3B_{1u} (c), and 1^3A_g (d) states in the linear H_4 model (Figure 1) calculated by the full configuration interaction (full CI)/STO-3G level of theory. Tables 1S, 2S, and 3S list the excited configurations in these states at closed-shell $[(R_1, R_2) [\text{\AA}] = (0.5, 0.5)]$, pure diradical $[(R_1, R_2) [\text{\AA}] = (4.0, 0.5)]$, and pure tetraradical $[(R_1, R_2) [\text{\AA}] = (4.0, 4.0)]$ regions, respectively. Figure 3S represents the variation in excitation energies from closed shell to pure diradical ($0.5 \text{ \AA} \leq R_1 \leq 4.0 \text{ \AA}$ at fixed $R_2 = 0.5 \text{ \AA}$, where $y_1 \sim 0$) (a), and from pure diradical to pure tetraradical limits ($0.5 \text{ \AA} \leq R_2 \leq 4.0 \text{ \AA}$ at fixed $R_1 = 4.0 \text{ \AA}$, where $y_0 \sim 1$) (b). As shown in Figure 2S, the $E(1^1B_{1u})$ is relatively insensitive to multiple diradical character compared to the other excitation energies, and also the $E(1^1B_{1u})$ has non-zero excitation energy in the whole region. This originates in its ionic bond character due to HOMO $\rightarrow$ LUMO singly excited configuration (see Tables 1S-3S) in contrast to the ground state, which could have the diradical $[(y_0, y_1) = (1, 0)]$ or tetraradical $[(y_0, y_1) = (1, 1)]$ characters. On the other hand, for $y_0 \sim 1$, the $E(2^1A_g)$ tends to decrease with increasing y_1 , and finally it becomes zero at $y_0 \sim y_1 \sim 1$ (see Figure 2Sb). This shows that the 2^1A_g state is described by the tetraradical wavefunction at $y_0 \sim y_1 \sim 1$ similar to the ground state. Indeed, the increase in the tetraradical character in the 2^1A_g state represents the increase in the weights of several doubly excited configurations of HOMO-1 $\rightarrow$ LUMO, HOMO $\rightarrow$ LUMO+1, and so on, as well as the HOMO $\rightarrow$ LUMO doubly excited configuration (see Tables 1S-3S). In addition, this tetraradical character in the 2^1A_g state is interpreted as the triplet-triplet coupled state with singlet spin multiplicity as is well known in polyenes [3]. It is also noted that the $E(2^1A_g)$ strongly depends on y_0 in the smaller y_0 region ($y_0 < \sim 0.2$) (see Figures 2Sb and 3Sa), the feature of which is characterized by the change in the dominant excited configurations, that is, from the (HOMO-1) $\rightarrow$ LUMO singly excited configuration in closed-shell $[(y_0, y_1) \sim (0, 0)]$ region to the linear combination of the ground and HOMO $\rightarrow$ LUMO doubly excited configurations in pure diradical $[(y_0, y_1) \sim (1, 0)]$ region (see Tables 1S and 2S). As shown in Figure 2Sc, the lowest triplet excitation energy $E(1^3B_{1u})$ significantly depends on y_0 and finally becomes zero in pure diradical ($y_0 = 1$) region. Because the 1^3B_{1u} state is regarded as the innate diradical state described by the singly excited configurations (see Tables 1S-3S), the excitation energy decreases with increasing the diradical character in the ground state. As a result, we have obtained $E(1^3B_{1u}) = 0$ at $y_0 \sim 1$. On the other hand, the second lowest triplet excitation energy $E(1^3A_g)$ strongly depends on y_1 (see Figure 2Sd). Indeed, the $E(1^3A_g)$ decreases with increasing y_1 , and finally becomes zero at $y_1 = 1$ (see Figures 2Sd and 3Sb). It is also noted that

$E(1^3A_g) \neq 0$ in diradical $[(y_0, y_1) \sim (1, 0)]$ region. These indicate that the 1^3A_g state is described by a tetraradical wavefunction in contrast to the innate diradical wavefunction for the 1^3B_{1u} .

As mentioned above, it is emphasized that the multiple diradical character (y_0, y_1) dependences of the excitation energies are responsible for the difference in the bond character between the ground and each excited state. Especially, the covalent (diradical or multiradical) bond character in excited states are found to strongly correlate with the (y_0, y_1) dependences of excitation energies. Here, one can recall that singlet fission essentially relates to the excited states with ionic and diradical/multiradical bond characters: the singlet states, 1^1B_{1u} (ionic) and 2^1A_g (tetraradical composed of triplet-coupled configuration) as well as the triplet states 1^3B_{1u} and 1^3A_g (which are the innate diradical and tetraradical triplet states, respectively). These results suggest that the feasibility conditions of singlet fission, $2E(T_1) \sim E(S_1)$ or $2E(T_1) < E(S_1)$ and $2E(T_1) < E(T_2)$, strongly correlate with multiple diradical character.

Figure 2S. Multiple diradical character (y_0, y_1) dependences of excitation energies of the 1^1B_{1u} , 2^1A_g , 1^3B_{1u} , and 1^3A_g states in the linear H_4 model (Figure 1). The dotted, dash-dotted, and solid lines represents the contour lines of $E = (0.1, 0.2)$, (0.3) , and $(0.4, 0.5)$, respectively.

Table 1S. Primary excitation configurations in the 1^1B_{1u} , 2^1A_g , 1^3B_{1u} , and 1^3A_g states at the closed shell limit $(y_0, y_1) \sim (0, 0)$, where $(R_1, R_2) [\text{\AA}] = (0.5, 0.5)$.

State	Configuration	Weight [%]
1^1B_{1u}	$h \rightarrow l$	99
2^1A_g	$h-1 \rightarrow l$	81
	$(h, h) \rightarrow (l, l)$	17
1^3B_{1u}	$h \rightarrow l$	69
	$h \rightarrow l+1$	28
1^3A_g	$(h-1, h) \rightarrow (l, l)$	45
	$(h-1, h) \rightarrow (l, l+1)$	45

Table 2S. Primary excitation configurations in the 1^1B_{1u} , 2^1A_g , 1^3B_{1u} , and 1^3A_g states at the pure diradical limit $(y_0, y_1) \sim (1, 0)$, where $(R_1, R_2) [\text{\AA}] = (4.0, 0.5)$.

State	Configuration	Weight [%]
1^1B_{1u}	$h \rightarrow l$	99
2^1A_g	Hartree-Fock ground	50
	$(h, h) \rightarrow (l, l)$	50
1^3B_{1u}	$h \rightarrow l$	49
	$h \rightarrow l+1$	15
	$h-1 \rightarrow l$	27
1^3A_g	$(h-1, h) \rightarrow (l, l)$	55
	$(h-1, h) \rightarrow (l, l+1)$	38

Table 3S. Primary excitation configurations in the 1^1B_{1u} , 2^1A_g , 1^3B_{1u} , and 1^3A_g states around the pure tetraradical limit $(y_0, y_1) \sim (1, 1)$, where $(R_1, R_2) [\text{\AA}] = (4.0, 4.0)$.

State	Configuration	Weight [%]
1^1B_{1u}	$h \rightarrow l$	36
	$(h-1, h-1, h) \rightarrow (l, l+1, l)$	31
2^1A_g	$(h-1, h-1) \rightarrow (l+1, l+1)$	12
	$(h, h) \rightarrow (l+1, l+1)$	23
	$(h-1, h) \rightarrow (l, l+1)$	25
	$(h-1, h-1) \rightarrow (l, l)$	23
	$(h, h) \rightarrow (l, l)$	13
1^3B_{1u}	$h-1 \rightarrow l$	21
	$h \rightarrow l+1$	22
	$(h-1, h-1, h) \rightarrow (l, l, l+1)$	21
	$(h-1, h, h) \rightarrow (l, l+1, l+1)$	21
1^3A_g	$(h-1, h) \rightarrow (l, l)$	25
	$(h-1, h-1) \rightarrow (l, l+1)$	25
	$(h, h) \rightarrow (l, l+1)$	25
	$(h-1, h) \rightarrow (l+1, l+1)$	25

Figure 3S. Variations in excitation energies of the 2^1A_g , 1^1B_{1u} , 1^3B_{1u} , and 1^3A_g states as the function of y_0 for $y_1 \sim 0$ (a) and of y_1 for $y_0 \sim 1$ (b).

3. Molecular structures of tetracene, 1,3-diphenylisobenzofran, pentacene, zexanthin, zethrene, PAH[2,5], and PAH[3,3]

Figure 4S. Molecular structures of tetracene (a), 1,3-diphenylisobenzofran (b), pentacene (c), zexanthin (d), zethrene (e), PAH[2,5] (f), and PAH[3,3] (g).

4. Calculation procedure of multiple diradical character using the PUHF method

The multiple diradical characters (y_i) are defined here as the occupation numbers of the LUNO+ i , where $i = 0, 1, \dots$ (LUNO = Lowest Unoccupied Natural Orbital) (see eq. s1 and Figure 1S) at the spin-projected spin-unrestricted Hartree-Fock (PUHF) level of theory, as proposed by Yamaguchi [1]. This is given by

$$y_i = 1 - \frac{2T_i}{1 + T_i^2} , \quad (s2)$$

where, T_i represents the orbital overlap between the corresponding orbital pairs, which is expressed in terms of the occupation numbers (n_i) of the UHF natural orbitals (UNOs) as

$$T_i = \frac{n_{\text{HONO}-i} - n_{\text{LUNO}-i}}{2} . \quad (s3)$$

The present scheme using the UNOs is the simplest but it can well reproduce the diradical characters calculated by other methods such as the ab initio configuration interaction method [4].

5. Relationship between experimental excitation energies and calculated multiple diradical characters

The experimental data for excitation energies of 1,3-diphenyliso-benzofran, tetracene, pentacene, and zeaxanthin are listed in Table 4S, as well as their multiple diradical characters of y_0 and y_1 calculated by the PUHF/6-31G* level of theory. As expected in the H_4 model, the energy difference $2T_1 - S_1$ tends to be lower as increasing the value of y_0 , while zeaxanthin have lower $2T_1 - S_1$ than pentacene. Zeaxanthin shows considerably smaller $2T_1 - T_2$, the feature of which is understood by the fact that it has relatively high multiple diradical characters of y_0 and y_1 value than others. Unfortunately, T_2 excitation energies of pentacene have not been observed in experiment due to the small oscillator strength between $T_1 \rightarrow T_2$ transition [13]. Although some data are missing in Table 4S, these results qualitatively indicates that the molecule with higher multiple diradical character tend to give lower values of $2T_1 - S$ and $2T_1 - T_2$ as expected in Figure 2, though zeaxanthin provides fairly lower values.

Table 4S. Experimental excitation energies (eV) and calculated diradical characters

State	1,3-diphenyliso-benzofran	Tetracene	Zeaxanthin	Pentacene
S^a	3.01 ^{f,i}	2.78 ^j	2.56 ^m	2.31 ^o
D^b	—	—	1.80 ⁿ	—
T_1^c	1.48 ^{g,i}	1.28 ^k	0.87 ⁿ	0.86 ^p
T_2^d	2.96 ^{h,i}	2.54 ^l	3.30 ^m	—
$D - S$	—	—	-0.76	—
$2T_1 - S$	-0.05	-0.23	-0.82	-0.59
$2T_1 - T_2$	0.00	0.01	-1.56	—
y_0^e	0.21	0.28	0.35	0.42
y_1^e	0.02	0.03	0.11	0.07

^a The lowest optically-allowed singlet excited state. ^b The lowest doubly excited state. ^c The lowest triplet excited state. ^d The second lowest triplet excited state, the excitation energy of which is obtained from the absorption spectra from T_1 state. ^e Multiple diradical character obtained by PUHF/6-31G* level of theory. ^f In 3-MP at 77 K. ^g In benzene solvent. ^h In DMSO solvent. ⁱ From ref. 5. ^j In argon gas from ref. 6. ^k In polymethylmethacrylate matrix at room temperature from ref. 7. ^l In alcoholic solution from ref. 8. ^m From ref. 9. ⁿ From ref. 10. ^o Gas phase from ref. 11. ^p In tetracene matrix at room temperature from ref. 12.

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