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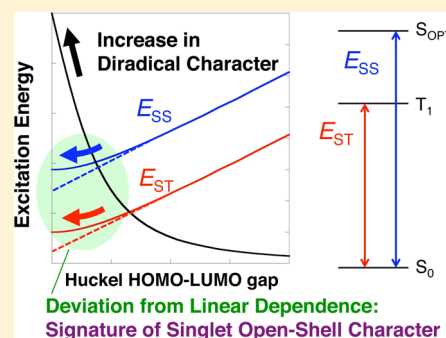
Signature of Singlet Open-Shell Character on the Optically Allowed Singlet Excitation Energy and Singlet–Triplet Energy Gap

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Supporting Information

ABSTRACT: A signature of singlet open-shell character on the optically allowed singlet excitation energy and singlet–triplet energy gap is theoretically illuminated for open-shell singlet molecules. On the basis of a two-site diradical model with two electrons in two orbitals, the linear dependence of these excitation energies on the transfer integral, which is equivalent to the energy gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals in the Hückel theory, is found to be broken down in the high diradical character region due to an increase in electron correlation in the open-shell singlet ground state. A series of polyacenes shows the similar behavior of the optically allowed singlet excitation energies obtained by time-dependent spin–flip density functional theory calculations and experiments, which bears testimony to the singlet open-shell character in long polyacenes.



1. INTRODUCTION

The optically allowed singlet excitation energy and singlet–triplet energy gap are two of the fundamental observables in chemistry, physics, and biology because they play an important role in several molecular properties, for example, optical absorptions, reflections, emissions, and molecular magnetism, which are utilized for a variety of applications such as light-emitting diodes,¹ photosensitizers,² nonlinear optical (NLO) materials,³ photochromic dyes,⁴ molecular magnets,⁵ and so on. In order to boost up these developments, a construction of novel molecular design principles for controlling excitation energies is indispensable.

The first useful principle for controlling molecular excitation energies was established in the Hückel theory, which provides an excitation energy as the difference between the occupied and virtual orbitals.⁶ Indeed, the energy gap between the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals exhibits linear dependences on experimental excitation energies for several hydrocarbons, as reported by Koutecký et al.⁷ In addition, the Hückel theory provides a well-known guideline for controlling excitation energies, that is, an increase in π -conjugation length leads to a decrease in excitation energy.⁶ In principle, however, excitation energies are known to depend not only on an orbital energy difference but also on the Coulomb and exchange integrals concerning occupied and virtual orbitals. Michl et al. explicitly indicated the importance of these additional quantities based on the discussion of the difference in the excitation energies between anthracene and azulene within a frame of the configuration interaction with single substitution (CIS) theory.⁸ However, this theory is only applicable to closed-shell molecules, which belong to the negligible or weak electron correlation regime

and are thereby described well by using a single Slater determinant.

On the other hand, electron correlations are indispensable for describing the electronic states of open-shell singlet molecules. For example, in a diradical molecular model with two electrons in two orbitals, its ground-state wave function is described by a multideterminantal form including a doubly excited determinant in addition to the Hartree–Fock (HF) ground-state determinant. The diradical character, which is theoretically defined,⁹ is known to be a useful quantitative chemical index for bond nature and electron correlations in the ground-state open-shell singlet molecules. Unfortunately, a viewpoint of diradical character for excitation energies of real open-shell singlet molecules has not been established yet, probably due to the difficulty of treating electron correlations in the open-shell singlet ground states. On the other hand, recent rapid developments of organic synthesis and physical fabrication technique enable us to realize various stable open-shell singlet molecules, for example, oligoacenes,^{10,11} diphenalenyl diradicaloids,¹² and zethrenes,¹³ and thus to measure their excitation energies and optical properties. These results are unveiling the peculiar structure–property relationships, which provide a novel picture of open-shell singlet states as well as an alternative way to realize highly effective functional materials in future photonics^{14–16} and spintronics.^{17,18} Now, we have to tackle the urgent task of constructing a novel chemical concept for the excitation energies of open-shell singlet molecules from the viewpoint of singlet open-shell character.

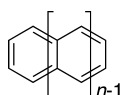
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First, we provide the analytical expressions of the first optically allowed singlet excitation energy, referred to as the singlet–singlet energy gap ($E_{SS} \equiv E_{S_1} - E_{S_0}$), as well as of the singlet–triplet energy gap ($E_{ST} \equiv E_{T_1} - E_{S_0}$) for a diradical model with two electrons in two orbitals, where S_0 , S_1 and T_1 indicate the singlet ground state, the lowest optically allowed excited state, and the lowest triplet state, respectively. The effect of electron correlations is discussed by comparing the excitation energies calculated by using the valence configuration interaction (VCI), the CIS, and the Hückel methods. In this study, the VCI method implies the full configuration interaction method considering only the two active electrons in two frontier orbitals.^{14,19} We also derive the analytical expressions of excitation energies as a function of diradical character (y) in order to clarify the relationship between the excitation energies and singlet open-shell character. Finally, the excitation energies of polyacenes (see Scheme 1) are investigated to confirm the validity of the present theoretical prediction.

Scheme 1. Polyacenes Examined in This Study ($2 \leq n \leq 12$)



2. METHODOLOGY

2.1. Excitation Energies and Diradical Character in a Two-Site Diradical Model. The analytical expressions of the excitation energies and diradical character for a diradical model¹⁴ are briefly explained as follows. As the simplest diradical system, 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) molecular orbitals (MOs) obtained by the highest spin (triplet in the present case) state spin-unrestricted (U) HF or density functional (DFT) method, the localized natural orbitals (LNOs) can be defined as²⁰

$$\begin{aligned} a(x) &= \frac{1}{\sqrt{2}}[g(x) + u(x)] \quad \text{and} \\ b(x) &= \frac{1}{\sqrt{2}}[g(x) - u(x)] \end{aligned} \quad (1)$$

LNOs are mainly localized on one site (A or B) with small tails on the other site and satisfy the orthogonal condition, $\langle ab| = 0$. By using LNO basis sets, E_{SS} and E_{ST} at the VCI and CIS level of theories are given by

$$\begin{aligned} E_{SS}^{\text{VCI}} &= -2K_{ab} + \frac{1}{2}(U + \sqrt{U^2 + 16t_{ab}^2}) \quad \text{and} \\ E_{ST}^{\text{VCI}} &= -2K_{ab} + \frac{1}{2}(-U + \sqrt{U^2 + 16t_{ab}^2}) \\ E_{SS}^{\text{CIS}} &= -2K_{ab} + \frac{1}{2}(U + 4|t_{ab}|) \quad \text{and} \\ E_{ST}^{\text{CIS}} &= -2K_{ab} + \frac{1}{2}(-U + 4|t_{ab}|) \end{aligned} \quad (2)$$

$$(3)$$

$U [=U_{aa} - U_{ab} \geq 0]$, where $U_{aa} = (a|a|a|a)$ (on-site Coulomb integral) and $U_{ab} = (a|a|b|b)$ (neighboring site Coulomb integral)] is an effective Coulomb repulsion, $K_{ab} [= (a|b|a|b) \geq 0]$ is a direct exchange integral, and t_{ab} is a transfer integral (the

derivations of eqs 2 and 3 are provided in Appendix A). Note that a transfer integral is approximately proportional to a $g-u$ energy gap, that is, the HOMO–LUMO energy gap (see eq B.5 in Appendix B). One finds the difference between eqs 2 and 3 in their third terms, while both of them coincide with each other when $|t_{ab}| \rightarrow \infty$ (negligible electron correlation), resulting in $(U^2 + 16t_{ab}^2)^{1/2} \rightarrow 4|t_{ab}|$. On the other hand, two electron integrals of U and K_{ab} are omitted in the Hückel method, and both E_{SS} and E_{ST} are thus equal to twice the absolute value of t_{ab} , which is equivalent to the HOMO–LUMO gap in the Hückel theory ($\Delta\epsilon_{\text{HL}}^{\text{Hückel}}$).

$$E_{SS}^{\text{Hückel}} = E_{ST}^{\text{Hückel}} = 2|t_{ab}| = \Delta\epsilon_{\text{HL}}^{\text{Hückel}} \quad (4)$$

Note that the VCI method provides a model exact solution including full electron correlations, while the CIS and the Hückel methods cannot describe electron correlations. In the VCI method, the diradical character y is defined as twice the weight of doubly excited configuration in the lowest singlet state ($=C_G|\bar{g}\bar{g}\rangle + C_D|u\bar{u}\rangle$), and is given by¹⁴

$$y = 1 - \frac{4|t_{ab}|}{\sqrt{U^2 + 16t_{ab}^2}} \quad (5)$$

where C_D is the coefficient of a doubly excited configuration in the lowest singlet state ($=C_G|\bar{g}\bar{g}\rangle + C_D|u\bar{u}\rangle$). As the weight of the doubly excited configuration is increased, a chemical bond is gradually weakened and is finally broken in the case of $|C_G| = |C_D| = 1/\sqrt{2}$. Therefore, $y = 2C_D^2 = 0$ and 1 indicate closed-shell and pure diradical ground states, respectively.

To illuminate the relationship between the excitation energies and diradical character (y), eq 2 is rewritten by substituting eq 5

$$\begin{aligned} E_{SS}^{\text{VCI}} &= \frac{U}{2} \left(1 + \frac{1}{\sqrt{1 - (1 - y)^2}} \right) - 2K_{ab} \quad \text{and} \\ E_{ST}^{\text{VCI}} &= \frac{U}{2} \left(-1 + \frac{1}{\sqrt{1 - (1 - y)^2}} \right) - 2K_{ab} \end{aligned} \quad (6)$$

which explicitly indicate that E_{SS}^{VCI} and E_{ST}^{VCI} are functions of three factors of U , K_{ab} , and y .

2.2. Computational Details. Geometries were optimized for S_0 and T_1 ($M_S = 0$) states by using the spin–flip (SF) time-dependent density functional theory (TDDFT) with the Tamm–Dancoff approximations²¹ (TDA) together with the collinear approximation.²² The BHHLYP functional (50% HF plus 50% Becke exchange²³ with Lee–Yang–Parr correlation²⁴) and 6-311G* basis sets were employed in this calculation because SF-DFT benchmark calculations show a better performance with hybrid functionals including a larger fraction of HF exchange than that with the conventional B3LYP functional.²² The reference states for the SF-DFT method (T_1 with $M_S = 1$ spin multiplicity) were obtained by using the restricted open-shell level of theories. Here, all atoms in polyacenes were put on the same molecular plane under the constraint of D_{2h} symmetry. To avoid a numerical instability of the noncollinear kernel,²⁵ the collinear approximation was employed for the geometry optimization.

The excitation energies of all polyacenes were calculated by using the long-range-corrected (LC)-BLYP/6-31G* method with the range-separating parameters of $\mu = 0.33$ bohr^{−126} in order to avoid the error in a global hybrid DFT for the HOMO

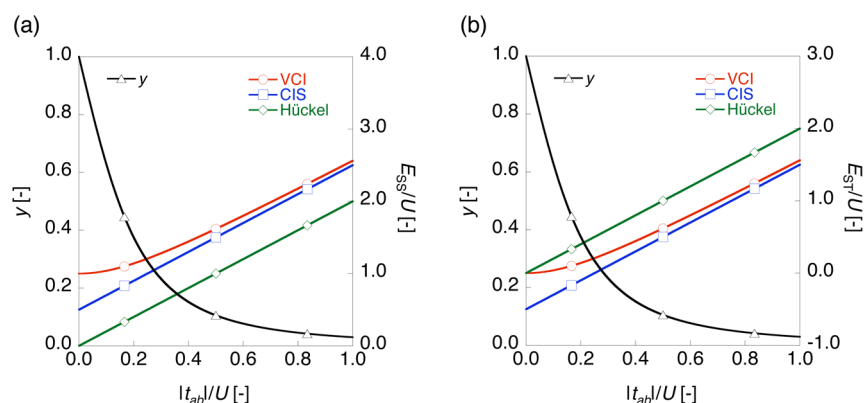


Figure 1. Variations in diradical character (y) and dimensionless excitation energies [E_{SS}/U (a) and E_{ST}/U (b)] obtained by VCI, CIS, and the Hückel calculations as a function of an absolute value of the dimensionless transfer integral ($|t_{ab}|/U$) in the two-site diradical model.

→ LUMO single-excitation energies of a series of acenes.²⁷ In this study, we employed three methods, (i) the TDDFT/TDA method with an S_0 reference state calculated by using the spin-restricted method (RDFT), (ii) the TDDFT/TDA method with a broken-symmetry solution for the S_0 reference state obtained by using the spin-unrestricted method (UDFT), and (iii) SF TDDFT/TDA with the noncollinear approximation (SFDFD).²⁸ For the SFDFD method, the reference states (T_1 with $M_S = 1$) were calculated by using the spin-unrestricted approach rather than the spin-restricted open-shell approach in order to evaluate the transfer integral (see eq 8). Fortunately, we found that the UDFT- and RODFT-based SFDFD methods give mutually almost the same results for the vertical excitation energies of polyacenes up to dodecacene (Figure 1S in the Supporting Information). Therefore, the spin contamination in the UDFT-based SFDFD calculation is negligible in the present system.

Effective Coulomb repulsions (U) and transfer integrals (t_{ab}) of polyacenes were estimated by using the UDFT and SFDFD methods combined with the following relationship

$$U = {}^1E_{HL} - {}^3E_{HL} \quad (7)$$

and

$$t_{ab} = -\frac{1}{2}\Delta\bar{\epsilon}_{HL}^T \quad (8)$$

where ${}^1E_{HL}$ and ${}^3E_{HL}$ denote the state energies of the singlet and triplet vertical excited states, both of which are mainly composed of HOMO → LUMO singly excited configurations (see eqs A.3 and A.4 in Appendix A), and $\Delta\bar{\epsilon}_{HL}^T$ is a HOMO–LUMO gap averaged over alpha and beta orbitals in a triplet state (see eq C.6 in the Appendix C).

Geometry optimization and R/UDFT calculations were performed by using the GAMESS program package,²⁹ and SFDFD calculations were done by using the Q-CHEM 4.0 program package.³⁰

3. VARIATIONS IN DIRADICAL CHARACTER AND EXCITATION ENERGIES AS A FUNCTION OF TRANSFER INTEGRAL

3.1. Two-Site Diradical Model. Figure 1a shows the variations in diradical characters and dimensionless E_{SS} ($=E_{SS}/U$) under the constraint of $2K_{ab}/U = 0.0$ as a function of the dimensionless transfer integral ($=|t_{ab}|/U$) (see eqs 2–4). Here, the y is shown to increase with the decrease in $|t_{ab}|/U$ according

to eq 5. Both CIS and Hückel E_{SS}/U values linearly depend on $|t_{ab}|/U$, though those amplitudes are different from each other due to the existence of the two-electron integrals (U and K_{ab}) in the CIS method but not in the Hückel method (see eqs 3 and 4). This linearly dependent behavior of the CIS method might be familiar to chemists similar to that in the Hückel theory (see eq 4). On the contrary, in the VCI method, which provides an exact solution in the present model, we found the deviation from the linear dependence of E_{SS}/U in the region with small $|t_{ab}|/U$ and large y . This noteworthy behavior in the VCI method is found to originate in the electron correlations in the ground state because the large value of y represents the large contribution of the doubly excited configuration (see eq 5), which implies strong electron correlations and causes the difference between the VCI and CIS results (see eqs 2 and 3). Therefore, the deviation from the linear dependence of E_{SS}/U on $|t_{ab}|/U$ is interpreted as the signature of an open-shell singlet character in the ground state. Similar behavior is found for E_{ST}/U due to almost the same expressions in eqs 2–4, though their absolute values are different from E_{SS}/U (see Figure 1b).

Figure 2 shows the variations in E_{SS}/U and E_{ST}/U for several values of $2K_{ab}/U$ as a function of diradical character (y). We

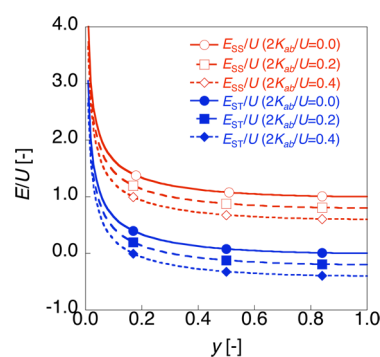


Figure 2. Variations in E_{SS}/U and E_{ST}/U as a function of diradical character (y) for different $2K_{ab}/U$ values at the VCI level of theory in the two-site diradical model.

found E_{SS}/U and E_{ST}/U decrease with the increase in y , while they converge to $1 - 2K_{ab}/U$ and $-2K_{ab}/U$, respectively, in the large y region (see eq 6). These excitation energies remain almost constant, ranging from intermediate to large y values, the behavior of which corresponds to the breakdown of linear dependences of E_{SS}/U and E_{ST}/U on $|t_{ab}|/U$ (see Figure 1a and b). It is also noted that the converged E_{SS}/U and E_{ST}/U at $y = 1$

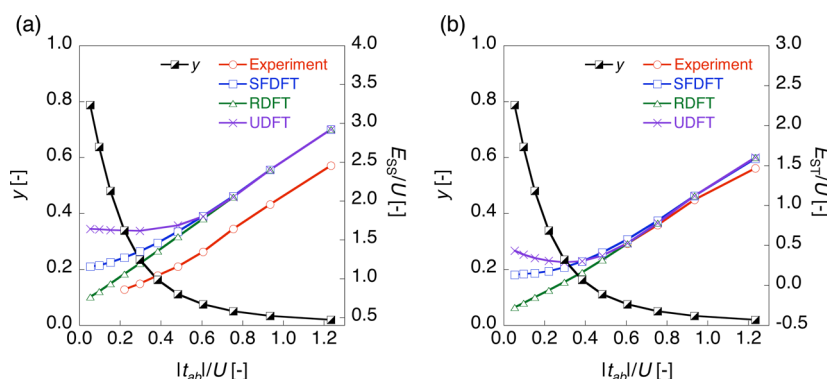


Figure 3. Variations in diradical character (y) and dimensionless excitation energies (E_{SS}/U and E_{ST}/U) obtained by the SFDFT, RDFT, and UDFT calculations as well as by experiments as a function of an absolute value of the dimensionless transfer integral ($|t_{ab}|/U$) for polyacenes ($2 \leq n \leq 12$).

decrease with the increase in K_{ab}/U , which indicates that the triplet ground state appears when a molecule has large y as well as large K_{ab}/U .

3.2. Polyacenes. To confirm the validity of the above electron correlation effect on the relationships between the diradical character, transfer integral, and excitation energies, we investigate the excitation energies of a series of polyacenes from naphthalene ($n = 2$) to dodecacene ($n = 12$) (see Scheme 1), in which open-shell singlet ground states are predicted for long polyacenes by Bendikov and co-workers.³¹ The spin-restricted (R), spin-unrestricted (U), and SF DFT methods were employed to evaluate the excitation energies. E_{SS} is evaluated by the vertical excitation energy of the singlet excited state mainly composed of the HOMO \rightarrow LUMO singly excited configuration with a strong oscillator strength, and E_{ST} is done by the adiabatic energy difference between the lowest singlet and triplet states. The parameters of U , $|t_{ab}|$, and y for polyacenes are evaluated by using the UDFT and SFDFT methods together with eqs 5, 7, and 8. Note here that $|t_{ab}|$ of a series of polyacenes is found to be proportional to the HOMO–LUMO gap in the singlet state (see Figure 2S in the Supporting Information), as expected by eq B.5 in Appendix B.

Figure 3a shows the variations of diradical character (y) and dimensionless E_{SS} ($=E_{SS}/U$) as a function of the dimensionless transfer integral ($|t_{ab}|/U$) for the polyacenes ($n = 2–12$) (see Tables 1S and 2S for the numerical data in the Supporting Information). In the region with large $|t_{ab}|/U$ and small y , we found that the experimental E_{SS}/U linearly depends on $|t_{ab}|/U$, as predicted by the Hückel theory.⁶ On the other hand, we found the deviation from the linear dependence of experimental E_{SS}/U on $|t_{ab}|/U$ in the region with small $|t_{ab}|/U$ and large y . To reveal the origin of this deviation from the linear dependence, we investigated the difference between the SFDFT and RDFT results because the former can describe a diradical ground state by involving an electron correlation through the doubly excited configuration,^{22,32} while the latter cannot. It is found that the SFDFT method provides the similar (E_{SS}/U)–($|t_{ab}|/U$) curve to the experimental one, whereas the RDFT method does not. These behaviors of the SFDFT and RDFT methods are similar to those of the VCI and CIS methods, respectively, in the two-site diradical model shown in Figure 1a. Namely, the difference between the SFDFT and RDFT results distinctly highlights the importance of an electron correlation for describing the ground state with non-negligible singlet open-shell character of the polyacenes from hexacene to dodecacene ($6 \leq n \leq 12$).

We here address the performance of the UDFT method, which has often been employed to investigate the electronic

structures of open-shell singlet molecules,³³ though it suffers from a spin contamination.³⁴ As shown in Figure 3a, the UDFT method succeeds in the qualitative description of the deviation from the linear dependence of E_{SS}/U on $|t_{ab}|/U$, while it overshoots the E_{SS}/U at the SFDFT level of theory in the large y region, probably due to an excess stabilization of the singlet ground state, which is caused by an excess orbital relaxation in extended variational space accompanied by a spin contamination. One may find that this result is in contrast to the success of the UDFT method combined with the finite-field (FF) method³⁵ for predicting the optical response properties such as the second hyperpolarizability of open-shell singlet molecules.³⁶ This would be understood by the fact that the FF method involves higher-order electron correlation effects accompanied by including electronic response to the external field³⁷ and is thus expected to remedy a part of the spin contaminations.³⁸

Figure 3b shows the variations in y and the dimensionless E_{ST}/U as a function of $|t_{ab}|/U$ for the series of polyacenes. The experimental E_{ST} values do not show the deviation from the linear dependence of E_{ST}/U on $|t_{ab}|/U$ yet because they are available only for $n < 5$. However, the SFDFT method is found to give a deviation from the linear dependence of E_{ST}/U on $|t_{ab}|/U$ in the region with small $|t_{ab}|/U$ and large y , whereas the RDFT does not. This behavior is shown to be consistent with that of E_{SS}/U , as expected from eqs 2 and 3. We thus conclude that the electron correlation in the open-shell singlet ground state of long polyacene ($n \geq 6$) causes the breakdown of linear dependence of E_{ST}/U on $|t_{ab}|/U$.

It is also noteworthy that the SFDFT method predicts a slightly positive value of E_{ST} for long polyacenes up to dodecacene ($n = 12$) with $y = 0.79$. According to eq 6 and Figure 2, a positive singlet–triplet gap at around $y = 1$ is predicted to be attributed to a small K_{ab} . Indeed, K_{ab} of an alternant hydrocarbon including a series of polyacenes is expected to be quite small due to the Coulson–Rushbrooke pairing theorem,³⁹ that is, the HOMO and LUMO of an alternant hydrocarbon have similar spatial distributions to each other except for the relative phase, which leads to small spatial overlap between the corresponding LNOs, resulting in small K_{ab} (see eq 1 and Figures 3S and 4S in the Supporting Information).

4. CONCLUSIONS

We have investigated the singlet open-shell character dependences of the optically allowed singlet excitation energy (E_{SS}) as

well as of the singlet–triplet energy gap (E_{ST}) based on the two-site diradical model. It was found that an electron correlation in the open-shell singlet ground state causes the breakdown of the linear dependence of E_{SS}/U and E_{ST}/U on the dimensionless transfer integral ($|t_{ab}|/U$), which is equivalent to the dimensionless HOMO–LUMO gap in the Hückel theory. This result is in contrast to the conventional (noncorrelated) theories such as the Hückel theory and the CIS, in which the singlet ground state is described by a single Slater determinant, referred to as the closed-shell state. This prediction has been confirmed by the $|t_{ab}|/U$ dependences of vertical E_{SS}/U and adiabatic E_{ST}/U of a series of polyacenes up to dodecacene. The present results provide a novel viewpoint of excitation energies based on the singlet open-shell character for open-shell singlet molecules, the view of which provides chemists with a new understanding basis as well as a new design concept of the excitation energies.

■ APPENDIX A. DERIVATIONS OF EQUATIONS 1 AND 2

In the VCI method for a system with two electrons in two orbitals, spatial symmetry-adapted orbitals (g and u , which have gerade and ungerade symmetries, respectively) obtained by the highest spin (triplet in the present case) state UHF/UDFT method relate to localized natural orbitals (LNO, a and b) through eq 1. For $M_S = 0$, there are two neutral $\{|a\bar{b}\rangle(\equiv|\text{core } a\bar{b}\rangle)$ and $|b\bar{a}\rangle(\equiv|\text{core } b\bar{a}\rangle)\}$ and two ionic $\{|a\bar{a}\rangle(\equiv|\text{core } a\bar{a}\rangle)$ and $|b\bar{b}\rangle(\equiv|\text{core } b\bar{b}\rangle)\}$ determinants, where “core” denotes the closed-shell core orbitals and the upper bar denotes the β spin. The configuration interaction matrix in the LNO representation $\{|a\bar{b}\rangle, |b\bar{a}\rangle, |a\bar{a}\rangle, \text{ and } |b\bar{b}\rangle\}$ is given by¹⁹

$$\begin{pmatrix} 0 & K_{ab} & t_{ab} & t_{ab} \\ K_{ab} & 0 & t_{ab} & t_{ab} \\ t_{ab} & t_{ab} & U & K_{ab} \\ t_{ab} & t_{ab} & K_{ab} & U \end{pmatrix} \quad (\text{A.1})$$

By diagonalizing this matrix, we obtain three singlet and one triplet eigenfunctions. The energies of a singlet ground state $|S_{1g}\rangle$, the lowest optically allowed singlet excited state $|S_{1u}\rangle$, and the lowest triplet state $|T_{1u}\rangle$ are given, respectively, by

$$^1E_{1g}^{\text{VCI}} = K_{ab} + \frac{U - \sqrt{U^2 + 16t_{ab}^2}}{2} \quad (\text{A.2})$$

$$^1E_{1u}^{\text{VCI}} = U - K_{ab} \quad (\text{A.3})$$

and

$$^3E_{1u}^{\text{VCI}} = -K_{ab} \quad (\text{A.4})$$

An optically allowed singlet excitation energy (E_{SS}) and singlet–triplet energy gap (E_{ST}) in the VCI method are therefore given by¹⁴

$$E_{SS}^{\text{VCI}} = ^1E_{1u}^{\text{VCI}} - ^1E_{1g}^{\text{VCI}} = -2K_{ab} + \frac{U + \sqrt{U^2 + 16t_{ab}^2}}{2} \quad (\text{A.5})$$

and

$$E_{ST}^{\text{VCI}} = ^3E_{1u}^{\text{VCI}} - ^1E_{1g}^{\text{VCI}} = -2K_{ab} + \frac{-U + \sqrt{U^2 + 16t_{ab}^2}}{2} \quad (\text{A.6})$$

On the other hand, in the CIS method, an energy of a singlet ground state is provided by the diagonal element of the Hamiltonian for the spin-restricted HF determinant $|g\bar{g}\rangle$

$$^1E_{1g}^{\text{HF}} = \langle g\bar{g} | \hat{H} | g\bar{g} \rangle = K_{ab} + \frac{U - 4|t_{ab}|}{2} \quad (\text{A.7})$$

where both the energies of the lowest optically allowed singlet state $|S_{1u}\rangle$ and those of the lowest triplet state $|T_{1u}\rangle$ in the CIS method are the same as those in the VCI method for a system with two electrons with two orbitals (eqs A.3 and A.4, respectively). As a result, we obtain CIS excitation energies.

$$E_{SS}^{\text{CIS}} = ^1E_{1u}^{\text{VCI}} - ^1E_{1g}^{\text{HF}} = -2K_{ab} + \frac{U + 4|t_{ab}|}{2} \quad (\text{A.8})$$

and

$$E_{ST}^{\text{CIS}} = ^3E_{1u}^{\text{VCI}} - ^1E_{1g}^{\text{HF}} = -2K_{ab} + \frac{-U + 4|t_{ab}|}{2} \quad (\text{A.9})$$

■ APPENDIX B. RELATIONSHIP BETWEEN THE TRANSFER INTEGRAL AND THE HOMO–LUMO GAP IN THE TWO-SITE DIRADICAL MODEL

In the VCI method for the system with two electrons in two active orbitals, a transfer integral (t_{ab}) is given by

$$\begin{aligned} t_{ab} &= \langle a\bar{b} | \hat{H} | b\bar{b} \rangle = \langle a | \hat{h} | b \rangle + \sum_c^{\text{core}} \langle a | c | b \rangle \langle c | b \rangle \\ &\quad + \langle a\bar{b} | b\bar{b} \rangle \\ &= h_{ab} + \langle a | b | b \rangle + \sum_c^{\text{core}} (2\langle a | c | b \rangle \langle c | b \rangle - \langle a | c | b \rangle \langle c | b \rangle) \end{aligned} \quad (\text{B.1})$$

On the other hand, the orbital energies of the HOMO (g) and LUMO (u) using the spin-restricted Fock operator f are given by

$$\epsilon_g^{\text{HF}} = \langle g | f | g \rangle = h_{gg} + J_{gg} + \sum_c^{\text{core}} (2\langle g | c | g \rangle \langle c | g \rangle - \langle g | c | g \rangle \langle c | g \rangle)$$

and

$$\begin{aligned} \epsilon_u^{\text{HF}} &= \langle u | f | u \rangle = h_{uu} + 2J_{gu} - K_{gu} \\ &\quad + \sum_c^{\text{core}} (2\langle u | c | u \rangle \langle c | u \rangle - \langle u | c | u \rangle \langle c | u \rangle) \end{aligned} \quad (\text{B.2})$$

which are similar to the bonding and antibonding MO energies, respectively, of singlet ground state calculated by the spin-restricted HF method. Thus, the orbital energy gap is expressed as

$$\begin{aligned} \Delta\epsilon_{gu}^{\text{HF}} &= \epsilon_u^{\text{HF}} - \epsilon_g^{\text{HF}} \\ &= (h_{uu} - h_{gg}) + 2J_{gu} - K_{gu} - J_{gg} \\ &\quad + \sum_c^{\text{core}} 2(\langle u | c | u \rangle \langle c | u \rangle - \langle g | c | g \rangle \langle c | g \rangle) \\ &\quad - (\langle u | c | u \rangle \langle c | u \rangle - \langle g | c | g \rangle \langle c | g \rangle) \end{aligned} \quad (\text{B.3})$$

which is rewritten by using the LNO basis set (see eq 1)

$$\Delta\epsilon_{gu}^{\text{HF}} = -2(h_{ab} + \langle ab|bb \rangle + \sum_c^{\text{core}} (2\langle ac|bc \rangle - \langle ac|cb \rangle)) + U_{ab} - 3K_{ab} \quad (\text{B.4})$$

By comparing eqs B.1 and B.4, we obtain

$$\Delta\epsilon_{gu}^{\text{HF}} = -2t_{ab} + U_{ab} - 3K_{ab} \quad (\text{B.5})$$

which shows $\Delta\epsilon_{gu}^{\text{HF}} \propto t_{ab}$ if $U_{ab} - 3K_{ab}$ is constant.

■ APPENDIX C. ESTIMATION OF THE TRANSFER INTEGRAL FROM THE BONDING AND ANTIBONDING MO GAP OF THE UHF TRIPLET STATE

In the spin-unrestricted HF (UHF) theory, the orbital energies of spatial symmetry-adapted MOs g and u with α and β spins are given by

$$\begin{aligned} \epsilon_g^\alpha &= h_{gg} + J_{gu} - K_{gu} + \sum_c^{\text{core}} (2\langle gclgc \rangle - \langle gclcg \rangle) \\ \epsilon_u^\alpha &= h_{uu} + J_{gu} - K_{gu} + \sum_c^{\text{core}} (2\langle ucluc \rangle - \langle uclcu \rangle) \end{aligned} \quad (\text{C.1})$$

$$\begin{aligned} \epsilon_g^\beta &= h_{gg} + J_{gg} + J_{gu} + \sum_c^{\text{core}} (2\langle gclgc \rangle - \langle gclcg \rangle) \\ \epsilon_u^\beta &= h_{uu} + J_{uu} + J_{gu} + \sum_c^{\text{core}} (2\langle ucluc \rangle - \langle uclcu \rangle) \end{aligned} \quad (\text{C.2})$$

where ϵ_i^θ denotes the i th orbital energy with θ spin function ($i = g$ or u , and $\theta = \alpha$ or β). The orbital energy gap for each spin is

$$\Delta\epsilon_{gu}^\alpha = \epsilon_u^\alpha - \epsilon_g^\alpha = h_{uu} - h_{gg} + \sum_c^{\text{core}} [2(\langle ucluc \rangle - \langle gclgc \rangle) - (\langle uclcu \rangle - \langle gclcg \rangle)] \quad (\text{C.3})$$

$$\begin{aligned} \Delta\epsilon_{gu}^\beta &= \epsilon_u^\beta - \epsilon_g^\beta = h_{uu} - h_{gg} + J_{uu} - J_{gg} \\ &+ \sum_c^{\text{core}} [2(\langle ucluc \rangle - \langle gclgc \rangle) - (\langle uclcu \rangle - \langle gclcg \rangle)] \end{aligned} \quad (\text{C.4})$$

The orbital energy gap ($\Delta\bar{\epsilon}_{gu}^T$) averaged over these α and β orbital gaps is given by

$$\begin{aligned} \Delta\bar{\epsilon}_{gu}^T &= \frac{1}{2}(\Delta\epsilon_{gu}^\alpha + \Delta\epsilon_{gu}^\beta) \\ &= h_{uu} - h_{gg} + \frac{1}{2}(J_{uu} - J_{gg}) \\ &+ \sum_c^{\text{core}} [2(\langle ucluc \rangle - \langle gclgc \rangle) - (\langle uclcu \rangle - \langle gclcg \rangle)] \end{aligned} \quad (\text{C.5})$$

The above equation is rewritten in the LNO basis representation by using eq 1

$$\begin{aligned} \Delta\bar{\epsilon}_{gu}^T &= -2(h_{ab} + \langle ab|bb \rangle + \sum_c^{\text{core}} (2\langle ac|bc \rangle - \langle ac|cb \rangle)) \\ &= -2t_{ab} \end{aligned} \quad (\text{C.6})$$

where we used eq B.1. In this study, although we employ spin-restricted and -unrestricted DFT methods, we approximately estimate t_{ab} using eq C.6. Namely, the present analysis is based on the VCI framework using Kohn–Sham orbitals obtained by using the LC-DFT methods.

■ ASSOCIATED CONTENT

Supporting Information

Dependence of vertical excitation energies on the reference wave function for the spin–flip density functional theory. Linear dependence of the HOMO–LUMO gap on the transfer integral in polyacenes. Numerical data used in Figure 3. Origin of small K_{ab} for polyacenes. Cartesian coordinates of geometries of polyacenes optimized by the SF-DFT/6-311G* using the BHHLYP functional with Tamm–Dancoff and noncollinear approximations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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