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Theoretical Study of Singlet Fission in Oligorylenes

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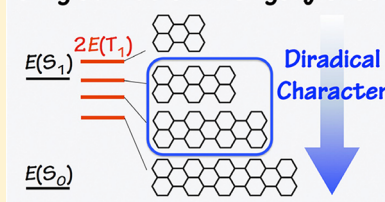
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S Supporting Information

ABSTRACT: Using the time-dependent tuned long-range corrected density functional theory method, the feasibility for singlet fission in oligorylenes has been investigated within the scope of the diradical character based guideline and of the energy level matching conditions for the isolated monomers. It is found that the relatively small-size oligorylenes, that is, terrylene and quaterrylene, which present intermediate diradical character without significant tetraradical character, are possible candidates for energetically efficient singlet fission. In relation to this result, we also raise the possibility that the unsettled ultrafast dynamics previously observed on quaterrylene is evidence for singlet fission.

SECTION: Molecular Structure, Quantum Chemistry, and General Theory

Singlet Fission in Oligorylenes



Singlet fission (SF) is the photochemical process where a singlet exciton splits into two triplet excitons.^{1–3} Recently, SF has attracted a great deal of interest both from science and engineering communities due to its possibility of overcoming the maximum limit of the photoelectric conversion efficiency of conventional photovoltaic cells (OPVs). This fascinating property originates in the multiple carrier generation from split triplet excitons⁴ as well as from the longer lifetime of triplet exciton than that of singlet one, which elongates the exciton diffusion length.⁵ At the present time, however, SF is known to occur in only a small number of molecules because most molecules have relatively large first triplet excitation energies [$E(T_1)$], which result in an endoergic SF process.

On the basis of the careful observation and analysis, Michl et al. have proposed the energy level matching conditions of SF, which should be satisfied by an isolated single molecule.^{3,6}

$$2E(T_1) - E(S_1) \approx 0 \text{ or } < 0 \quad [\text{condition (i)}] \quad (1)$$

$$2E(T_1) - E(T_2) \leq 0 \quad [\text{condition (ii)}] \quad (2)$$

Condition (i) is necessary for the split of a singlet exciton (S_1) into two triplet excitons (T_1), while condition (ii) is for suppressing the triplet–triplet annihilation, which generates a singlet ground state (S_0) and a higher triplet state (T_2) from the two split triplet excitons (T_1). Although these conditions ignore the effects of intermolecular interactions, nonadiabatic transitions, and geometry changes, in real SF dynamics,^{3,7–9} eqs 1 and 2 are known to be quite useful for prescreening of efficient SF molecules.⁶ Indeed, Michl et al. have proposed two kinds of candidate systems based on these conditions,^{3,6} (A) alternate hydrocarbons with large exchange integrals K_{HL} concerning the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which approximately describe the energy differences between S_1 and T_1 when both states are characterized by the HOMO \rightarrow LUMO one-electron transition, and (B) diradicaloids, which

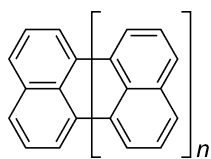
are expected to have small energy differences between S_0 and T_1 . In our previous study,¹⁰ we have highlighted the importance of the diradicaloids from the viewpoint of the multiple diradical character based guideline deduced from the full configuration interaction calculations of tetraradical model systems¹¹ and have demonstrated that molecules with small/intermediate diradical character are the candidates of energetically efficient singlet fission [$2E(T_1) - E(S_1) \approx 0$]. Furthermore, on the basis of this guideline, we have predicted that the relatively small size polycyclic aromatic hydrocarbons (PAHs) including terrylene (which was referred to as PAH[2,5] in ref 10) are promising candidates for SF. However, there have been few reports on SF in oligorylenes, except for perylenes, in which SF is known to occur from high-lying singlet excited states.¹² On the other hand, oligorylenes are known to have thermostability at ambient conditions and to have high absorption coefficients for the lowest-lying optically allowed excited states,^{13–17} which are the desired properties in application to optoelectric devices such as OPVs. In order to confirm our previous prediction and to illuminate the structural dependences of oligorylenes on the energy level matching conditions (eqs 1 and 2), we investigate the excitation energies of S_1 , T_1 , and T_2 states as well as the multiple diradical characters y_0 and y_1 of the relatively small size oligorylenes, that is, perylene, terrylene, quaterrylene, and pentarylene (Scheme 1). The excitation energies are calculated using the time-dependent tuned long-range corrected density functional theory (TD-tuned-LC-BLYP) method,¹⁸ while the multiple diradical characters are evaluated using the spin-projected unrestricted Hartree–Fock (PUHF) method^{19,20} (see the Computational Details and Supporting Information). On the basis of the present result, we also raise the possibility that the unsettled ultrafast dynamics previously observed in the

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Scheme 1. Oligorylenes [Perylene ($n = 1$), Terrylene ($n = 2$), Quaterrylene ($n = 3$), and Pentarylene ($n = 4$)]



transient absorption spectrum of quaterrylene is evidence for SF. The present study not only demonstrates the performance of the diradical character based guideline but also proposes a novel class of promising candidates, oligorylenes, for efficient SF.

First, the reliability of the TD-tuned-LC-BLYP method is discussed by comparing the calculated vertical excitation energies with the corresponding experimental values. Here, we have examined the oligorylenes with no substituents and no solvation effects for simplicity, though the experimental values are obtained for tetra-*t*-butyl-substituted oligorylenes in 1,4-dioxane solution. Such simplification is justified by the fact that tetra-*t*-butyl substitution and solvent effects are negligibly small (less than 0.12 eV), as confirmed by our preliminary calculation in perylene (see Table 1S in the Supporting Information). Table 1 lists the excitation energies and optical absorption

Table 1. Excitation Energies and Properties of the First Optically Allowed Excited States

molecules	experiment ^a		calculation ^b	
	E [eV]	ϵ^c [l/mol·cm]	E [eV]	f^d [–]
perylene ($n = 1$)	2.82	28000	3.04	0.40
terrylene ($n = 2$)	2.21	65000	2.29	0.76
quaterrylene ($n = 3$)	1.88	138000	1.88	1.17
pentarylene ($n = 4$)	1.64	– ^e	1.60	1.62

^aReference 21 for tetra-*t*-butyl substituted oligorylenes in 1,4-dioxane solution. ^bCalculated using the TD-tuned-LC-RBLYP/6-31+G* method. ^cMolar absorbance coefficient. ^dOscillator strength. ^eNot observed due to the low solubility.

properties concerning the first optically allowed excited states. The experimental values are quoted from ref 21, reported by Müllen et al. We found that the theoretical (theor.) results reproduce the experimental (exp.) ones well; excellent agreement between both excitation energies within an error of 0.2 eV and dramatic increases of the oscillator strengths f (theor.) as well as of the optical absorption strengths ϵ (exp.) with the increase in the molecular size from perylene to quaterrylene is seen. These results indicate that the TD-tuned-LC-BLYP/6-31+G* method works well for describing the optically allowed excited states of relatively small size oligorylenes.

Table 2 gives the calculated results of multiple diradical characters (y_0 and y_1 , which are the indices of the diradical and tetraradical natures, respectively¹⁰), of the vertical excitation energies, $E(S_1)$, $E(T_1)$, and $E(T_2)$, and of the left-hand sides of the energy level matching conditions (i) and (ii) (see eqs 1 and 2). The main configurations and the related MOs in each state are shown in Table 3S and Figures 2S–5S, respectively, in the Supporting Information. Noted that there is no triplet instability problem leading to a too low T_1 excitation energy.²² Indeed, both S_1 and T_1 excitation energies listed in Table 2 are found to almost coincide with those evaluated by the single

Table 2. Diradical Characters^a (y_0 , y_1), Vertical Excitation Energies^b [eV], and the Left-Hand Sides of Energy Level Matching Conditions (i) and (ii) (Equations 1 and 2)

	perylene ($n = 1$)	terrylene ($n = 2$)	quaterrylene ($n = 3$)	pentarylene ($n = 4$)
y_0	0.21	0.37	0.48	0.57
y_1	0.02	0.05	0.11	0.17
$E(S_1)$	3.04	2.29	1.88	1.60
$E(T_1)$	1.67	1.10	0.80	0.58
$E(T_2)$	3.17	2.33	1.78	1.41
$2E(T_1) - E(S_1)$	0.31	−0.08	−0.28	−0.44
$2E(T_1) - E(T_2)$	0.17	−0.13	−0.19	−0.25

^aObtained from the occupation numbers of UNO/6-31+G*.

^bCalculated using the TD-tuned-LC-RBLYP/6-31+G* method.

spin–flip DFT, which is expected to quantitatively reproduce the first triplet excitation energies of open-shell singlet molecules,²³ though it cannot evaluate the T_2 excitation energy correctly due to the lack of its spin-adopted configuration within the single spin–flip scheme (see Table 4S in the Supporting Information).

We found that all of the oligorylenes examined in this study have intermediate y_0 and small y_1 values, though they show similar size dependences, that is, the larger the size (n), the larger the y_i . This result indicates that all of these systems are categorized as the intermediate diradical molecules. It is noted that the lowest triplet excitation energies [$E(T_1)$] rapidly decrease with the increase in the molecular size (n) as compared to the other excitation energies [$E(S_1)$ and $E(T_2)$], the feature of which results in the decreases in $2E(T_1) - E(S_1)$ and $2E(T_1) - E(T_2)$ with the increase in the molecular size. This tendency agrees with our previous results based on the full configuration interaction H_4 model,¹⁰ that is, $E(T_1)$ tends to decrease with the increase in the diradical character (y_0). In fact, in perylene, which presents a relatively small diradical character ($y_0 = 0.21$), it is difficult for SF to occur from the lowest-lying singlet excited state S_1 due to the positive value of $2E(T_1) - E(S_1)$, and even if SF occurs in perylene, the split triplet excitons will be recombined easily due to the positive value of $2E(T_1) - E(T_2)$. Here, both of those positive values are predicted to be caused by the high $E(T_1)$ value originating from the relatively small diradical character of perylene. Also, pentarylene, which presents a relatively large diradical character, is not predicted to be suitable for energetically efficient SF, though it satisfies both energy level matching conditions (i) and (ii) because the energy loss in the SF process [represented by $|2E(T_1) - E(S_1)|$] becomes large due to the too small $E(T_1)$ value. On the other hand, the intermediate-size oligorylenes, that is, terrylene and quaterrylene, are found to satisfy the energy level matching conditions (i) and (ii), as well as the relatively small energy loss in the SF process. Thus, terrylene and quaterrylene are predicted to be promising candidates of energetically efficient SF. Further detailed discussion on the effect of the doubly excited configurations and the reliability of the TD-tuned-LC-BLYP method for the evaluation of the energy level matching conditions is presented in the Supporting Information (see Tables 7S and 8S).

Finally, we address the unsettled ultrafast excitation dynamics previously observed in quaterrylene.²⁴ In the transient absorption spectrum of quaterrylene in THF solution, Müllen et al. have observed the ultrafast (500 fs) transition from S_1 to the intermediate state (X), which finally leads to the long-lived

state (Y) with the lifetime of 1 ns. The origin of this ultrafast transient dynamics has not been clarified in the previous study. However, provided that the long-lived final state is the T_1 state, one finds that this ultrafast excitation dynamics in quaterylene shares quite similar character to that in SF. As is well-known, SF could produce the lowest-lying triplet excitation in several picoseconds^{25–28} due to the spin-allowed transition from $S_1 + S_0$ to $^1(T_1T_1)$, where the former denotes that there is one singlet exciton, while the latter indicates a coupled double–triplets state, that is, a singlet state as a whole. In fact, the ultrafast emergence of a triplet–triplet absorption in a transient absorption spectrum is often considered as the characteristic signal of SF.^{29–32} It is noted that although the transient absorption experiment has been performed in solution, quaterrylenes tend to easily aggregate with each other in a low dielectric solution due to their low solubility, as mentioned by Müllen et al.²⁴ This aggregation is expected to cause SF through intermolecular interactions. Furthermore, our present calculation predicts that SF occurs in quaterylene aggregates from the viewpoint of the energy level matching conditions (see Table 2), though these values are evaluated for the isolated monomer. In order to further confirm our prediction, we have evaluated the optical absorptions of the T_1 state (see Table 3).

Table 3. $T_1 \rightarrow T_n$ Vertical Excitation Energies (E in eV) and Oscillator Strengths (f)^{a,b}

state	perylene ($n = 1$)		terrylene ($n = 2$)		quaterylene ($n = 3$)		pentarylene ($n = 4$)	
	E [eV]	f [–]	E [eV]	f [–]	E [eV]	f [–]	E [eV]	f [–]
T_2	1.59	0.00	1.50	0.00	1.19	0.00	1.02	0.00
T_3	1.87	0.00	1.74	0.00	1.79	0.01	1.65	0.00
T_4	2.16	0.00	2.26	0.00	2.00	1.40	1.75	1.91
T_5	2.37	0.00	2.34	0.08	2.00	0.00	1.83	0.01
T_6	2.37	0.03	2.40	0.95	2.27	0.05	2.25	0.06
T_7	2.64	0.14	2.49	0.00	2.30	0.01	2.27	0.00
T_8	2.84	0.00	2.61	0.00	2.51	0.00	2.32	0.00
T_9	2.96	0.49	2.64	0.00	2.56	0.00	2.35	0.00
T_{10}	3.43	0.00	2.72	0.00	2.71	0.00	2.44	0.00
T_{11}	3.45	0.00	3.01	0.00	2.76	0.00	2.51	0.00

^aCalculated using the TD-tuned-LC-UBLYP/6-31+G* method.

^bGeometries are optimized for T_1 states using the UB3LYP/6-311G* method.

The detailed results of the excited configurations and of $\langle S^2 \rangle$ values of excited states are listed in Tables S5 and S6 in the Supporting Information. The reliability of our calculations is confirmed by the comparison between the theoretical and experimental excitation energies of terrylene; we found the calculated strong absorption at the $T_1 \rightarrow T_6$ transition (2.40 eV), which agrees well with the experimental $T_1 \rightarrow T_n$ transition at 541 nm (2.29 eV).²⁴ Similarly, in quaterylene, the calculated strong absorption at the $T_1 \rightarrow T_4$ transition (2.00 eV) corresponds to the experimental optical absorption at 649 nm (1.91 eV) of the unsettled final state (Y).²⁴ It is therefore predicted that the previously observed final state (Y) in the transient absorption spectrum of quaterylene is the lowest-lying triplet excited state (T_1). These results strongly support our prediction that the previously observed unsettled dynamics in quaterylene is evidence for singlet fission. To confirm our prediction by clarifying this transient dynamics, both experimental and theoretical investigations, for example, the magnetic response experiment³³ and the explicit time domain

simulation using ab initio dynamics simulation,³⁴ will be required.

In summary, we have shown that relatively small size oligorylenes with weak/intermediate diradical character, that is, terrylene and quaterylene, are suitable for energetically efficient SF based on the energy level matching conditions using the TD-tuned-LC-BLYP¹⁸ and PUHF^{19,20} methods. The present results also demonstrate the validity of our molecular design guideline based on the multiple diradical character.¹⁰ In addition, the present results illuminate the possibility that the previously observed unsettled ultrafast dynamics in the transient absorption experiment on quaterylene²⁴ is evidence for SF. To confirm the transient dynamics indicating SF, we need further investigation, such as the magnetic response experiment,³³ or the kinetics of the excitation dynamics.^{7–9,34} These predictions will stimulate the experimentalists to investigate SF in oligorylenes and thus pave the way toward the more fundamental understanding of the relationship between molecular structures and SF, which leads to progress in developing efficient OPVs utilizing SF.

■ COMPUTATIONAL DETAILS

The geometries of the singlet ground (S_0) and the first triplet excited (T_1) states were optimized at the RB3LYP/6-311G* and UB3LYP/6-311G* levels of theory, respectively. The geometrical symmetries were fixed to be D_{2h} , except for perylene, which was found to have the minimum-energy structures with D_2 and C_2 symmetries for S_0 and T_1 states, respectively.

The multiple diradical characters (y_i) of these molecules are evaluated as the occupation numbers of the i -th lowest unoccupied natural orbitals ($n_{\text{LUNO}+i}$),³⁵ for example, y_0 and y_1 are the occupation numbers of LUNO and LUNO+1, respectively. From this definition, y_i takes a value between 0 and 1, which indicate closed-shell and pure open-shell states, respectively, with the relation of $y_i \geq y_{i+1}$. For example, $(y_0, y_1) = (0, 0)$, $(1, 0)$, and $(1, 1)$ represent the closed-shell, pure diradical, and pure tetraradical states, respectively. The spin-projected unrestricted Hartree–Fock (PUHF) method^{19,20} is employed to evaluate the multiple diradical characters³⁵ (see section 8 in the Supporting Information) because the PUHF method can effectively remove the spin contamination effects on the occupation numbers.

The excited states are evaluated using the time-dependent density functional theory (TD-DFT) method. We have employed the tuned-LC-BLYP functional, the range-separation parameter of which is properly tuned so as to satisfy one of the exact conditions in DFT [$\epsilon_{\text{HOMO}}(N) = -\text{VIP}(N)$]¹⁸ (see section 9 in the Supporting Information). The tuned-LC-DFT method has previously succeeded in the quantitative reproduction of the one-electron excitation energies with low computational costs.^{36,37} The tuned parameters for oligorylenes are listed in Table S2 in the Supporting Information. The TD-tuned-LC-RBLYP and TD-tuned-LC-UBLYP methods are employed for the calculations of the vertical excitation energies from the S_0 and T_1 states, respectively. It is noted that so-called open-shell singlet (spin-unrestricted) solutions are not obtained for S_0 states in the present calculations, which implies that the triplet instability problem is not observed in these molecular systems at the tuned-LC-BLYP level of theory. Indeed, DFT is known to suffer from less spin contamination than that at the Hartree–Fock level of theory.³⁸ On the basis of the discussion on the reliability of the TD-tuned-LC-BLYP through the

comparison with the experimental results of the oligorylenes, as well as on the contribution of doubly excited configuration to the excited states using the multireference second-order perturbation theory, we have concluded that the TD-tuned-LC-BLYP method is useful for semiquantitative evaluation of the energy level matching conditions for the present molecular systems, at least, with up to the size examined in this study (see section 10 in the Supporting Information).

The 6-31+G* basis sets were employed in PUHF and TD-tuned-LC-BLYP calculations. All of the calculations were performed using the Gaussian09 program package.³⁹

■ ASSOCIATED CONTENT

■ Supporting Information

Substituent and solvation effects on the low-lying vertical excited states of perylene. Tuned range separating parameters in LC-BLYP/6-31+G* for oligorylenes. Excitation configurations in $S_0 \rightarrow S_n$ (T_n) transitions of oligorylenes. Molecular orbitals relating to the main configurations in $S_0 \rightarrow S_n$ (T_n) transitions of oligorylenes at the TD-tuned-LC-BLYP/6-31+G* level of theory. Comparison of the excitation energies calculated using the time-dependent density functional theory (TD-DFT) method and the spin-flip density functional theory method with the Tamm–Dancoff approximation (SF-DFT/TDA). Excitation configurations in $T_1 \rightarrow T_n$ transitions of oligorylenes. $\langle S^2 \rangle$ values for T_n ($n \geq 2$) states of oligorylenes obtained by $T_1 \rightarrow T_n$ transition calculations at the TD-tuned-LC-BLYP/6-31+G* level of theory. Calculation procedure of multiple diradical character using the PUHF method. Tuning scheme of the range separating parameter in the tuned-LC-BLYP method. Discussion of the applicability of the TD-tuned-LC-BLYP method to the evaluation of the energy level matching conditions for the oligorylenes examined in this study. 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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