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Kyoto University
Exploration of Quenching Pathways of Multiluminescent Acenes Using the GRRM Method with the SF-TDDFT Method

Satoshi Suzuki, Satoshi Maeda, and Keiji Morokuma

Abstract: The quenching pathways were investigated for three types of multiluminescent acene derivatives, which show environment-dependent fluorescence. Spin-flip time-dependent density functional theory (SF-TDDFT) combined with the Global Reaction Route mapping (GRRM) strategy is employed to locate minimum-energy conical intersections (MECIs). The energies and geometries of the MECIs relative to the Franck–Condon (FC) state control the difference in fluorescence behavior among the three derivatives. For the molecule with a phenyamide moiety, a MECI with energy lower than the FC state with large geometrical change from V-type to flat structure provides an efficient internal conversion (quenching) pathway in solution. For the same molecule, in a solid, this large geometrical change is inhibited, and the second MECI, with an energy lower than FC but higher than the first MECI requiring only a small geometry change of CH out-of-plane bending, contributes to the quenching. The molecule with the napthaleneimide moiety has only one low-energy MECI that requires large geometrical change from the V-type to flat structure. Although this MECI provides the quenching pathway in solution, in the solid, this large motion is inhibited, and the molecule will stay in the excited state and emit. The molecule with an anthraceneimide moiety has no conical intersection lower than the FC state, and no quenching pathway is available in solution or solid. In addition, in this molecule, at the local minimum of the excited state, the dipole transition to the ground state is allowed, and this molecule prefers emission rather than internal conversion.

1. Introduction

Owing to their optical and electronic properties, π-conjugated systems have attracted much attention as a functional material. Recently, a series of π systems that consists of a flexible cyclooctatetraene (COT) core and aceneimide wings with different conjugation lengths has been synthesized. This system exhibits bent-to-planar conformal change in the excited state. A significant feature of this system is to show environment-dependent fluorescence from a single-component fluorophore. The system gives a blue emission from the V-shaped structure in a polymer matrix or in a frozen solution, a green emission from the planar geometry in solution, and a red emission in the crystalline state. The molecule with anthraceneimide wings is emissive both in solution and in the solid state, while the molecule with phenylenemide has no emission either in solution or in the solid state. For the molecule with a napthaleneimide moiety, although no fluorescence is observed in the various common organic solvents at room temperature, the compound shows fluorescence in the solid state. The different emission behavior for different acenes has been explained by the difference in the transition dipole moment (TDM). The TDM of phenylenemide and naphthaleneimide at the S₁ minimum is zero due to symmetry, while that of anthraceneimide at the S₁ minimum has a finite value. TDM explains why the molecule with an anthraceneimide wing is emissive. However, the difference between phenylenemide and napthaleneimide cannot be explained by TDM.

In many photochemical processes such as photochemical reactions and fluorescence quenching, the conical intersections (CIs) play an important role because nonadiabatic transitions from excited states to the ground state take place very efficiently in the vicinity of the CI. The CI between two electronic states forms an (f−2)-dimensional hypersurface, while individual potential energy surfaces (PESs) form f-dimensional hypersurfaces, where f is the internal degree of freedom of a system. Although nonadiabatic transition can take place anywhere near the CI surface, the energy local minimum on the CI hypersurface, the minimum-energy CI (MECI), is a critical point below which CI does not exist and nonadiabatic transition cannot easily take place. In fluorescence, there will be competition between the emission from the local minimum of the excited state controlled by the TDM and quenching through CIs that depends on their geometry, energy, and...
nonadiabatic coupling element. If the path from the Franck-Condon (FC) region to reach a CI is downhill or has a low enough barrier, quenching can compete efficiently with fluorescence.

In order to explain the difference in emission behavior of the present molecules, we explored and located MECIs between $S_1$ and $S_0$ for the three aceneimides 1–3 in Figure 1 and determined possible quenching pathways, starting from the FC region, with the GRRM (Global Reaction Route Mapping) strategy,9–15 which consists of two independent automatic global search methods, ADDF and AFIR (see ref 12 in detail). The difference in quenching pathway among the three systems would lead to the difference of emission behavior.

Time-dependent density functional theory (TDDFT) is a powerful tool for describing excited states. Among the wave function theories, the multiconfigurational space self-consistent field (MCSCF) method, such as the complete active space self-consistent field (CASSCF), and the multireference perturbation theory, such as the second-order complete active space perturbation theory (CASPT2)16 and multiconfigurational quasidegenerate perturbation theory (MCQDPT),17 have been widely used to calculate excited states. CASSCF lacks dynamic correlation and sometimes fails to describe electronic structure properly. The multireference perturbation theory includes dynamic electronic correlation and is usually reliable, but its computational cost is sometimes too large to apply to large molecular systems.

On the other hand, TDDFT is very useful for many cases owing to its “acceptable” accuracy and low computational cost.

In the linear response (LR)-TDDFT, excitation energies are determined as poles of the response function. Because the ground state and excited states are treated in a different way, the CI between them cannot be determined in the TDDFT method.

Recently, it has been shown that spin–flip (SF)-TDDFT has a potential ability to obtain the correct CI.18–21 In SF-TDDFT, $S_0$ and $S_1$ states are expressed as excited states from the reference lowest triplet $T_1$ state that is obtained in the unrestricted Kohn–Sham (UKS) or restricted open-shell Kohn–Sham (ROKS) equation. In the present calculation, ROKS is employed. A significant fault of the SF-TDDFT method is that it often gives spin-contaminated states. To deal with this problem, we checked $(S^2)$ and the CI coefficients during the optimization. Details are described in a later section.

Section 2 describes the theoretical background and computational methods. In section 3, quenching pathways of each molecule are determined and discussed. The conclusion is given in section 4.

2. METHODS AND COMPUTATIONAL DETAILS

In the experiment, $n$-butylimides are used. In the present study, $n$-butyl groups are replaced by hydrogens. Preliminary calculations suggested that the effect of $n$-butyl on the structure and excitation energies is not very significant. For instance, the lowest excitation energy is 2.73 eV with $n$-butyl, while it is 2.72 eV with H. Therefore, this replacement can be justified for qualitative discussion. The equilibrium geometry of each molecule in the $S_0$ state was optimized at the B3LYP/6-31+G(d) level. Starting from the $S_0$ equilibrium geometry, the local or global minimum (MIN) for the $S_1$ state is optimized with TD-B3LYP/6-31+G(d). Throughout the paper, energies and gradients were computed by the GAMESS program.

It turns out that starting the MECI search from the FC geometry by using SF-TADDFT is not necessarily the most efficient as the geometry of MECI is often substantially different from that of the FC geometry and SF-TADDFT states change their nature during optimization. Instead, we used standard restricted and unrestricted DFT methods to calculate $S_0$ and $T_1$ states, respectively, and located the approximate minimum-energy point on the seam of crossing (MESX) between $S_0$ and $T_1$. One expects that $S_0$ and $T_1$ states have similar shape of potential surfaces if they have the same electron configuration (except for spin). Thus, the $S_1/S_0$ MECI search from $S_0/T_1$ MESX is finished with a small number of iterations. This MESX search requires only standard DFT calculations for the lowest singlet and lowest triplet states and avoids SF-TADDFT excited-state calculations. After MESXs were obtained, we searched the $S_1/S_0$ MECI from each $S_0/T_1$ MESX.

MESXs are located by adopting the ADDF (anharmonic downward distortion following) search method for the seam model function (SMF) method implemented in the GRRM program.22 It is worth noting that ADDF search is a method to obtain all possible local minima on a PES. Thus, when we apply the ADDF method to SMF, we can locate many lowest local minima on SMF.

SMF is a function

$$\mu_{\text{SMF}}(Q) = \frac{1}{2} \left[ E_{\text{State}-1}(Q) + E_{\text{State}-2}(Q) \right] + \frac{E_{\text{State}-1}(Q) - E_{\text{State}-2}(Q)}{\alpha}$$

(1)

consisting of a mean energy term for the two target PESs, $E_{\text{State}-1}(Q)$ and $E_{\text{State}-2}(Q)$, and a penalty function for their energy difference. $Q$ represents the atomic coordinates $(Q_i)$, and $\alpha$ is a constant parameter. Minima of SMF correspond to approximate MESX geometries. For each molecule independently, we obtained all important MESXs without guess using a combination of the SMF and ADDF approach. From all of these MESXs (including ones with energy higher than $S_1$ FC), we optimized MECIs. Thus, it is very unlikely that any important MECI is missed. SF-TDB3LYP/3-21G was used for the initial MESXs search, and $S_0/S_1$ MECIs were reoptimized using the branching plane updating method14 at the SF-TDB3LYP/6-31+G(d) level, all using the GRRM program.

Energies and gradients of the $S_0$ and $S_1$ states were calculated

Figure 1. Chemical structure of aceneimide compounds 1–3.
using the SF-TDDFT method with the Tamm–Dancoff approximation implemented in the GAMESS program package. In the SF-TDDFT calculation, the reference triplet state was obtained by the ROKS equation.

One significant fault of SF-TDDFT is that it gives spin-contaminated states. Although expectation values of the total spin-squared operator, namely, \( \langle S^2 \rangle \), sometimes fluctuate between 0.0 and 2.0, which correspond to pure singlet or triplet states, they often become around 1.0, which indicates strongly mixed states. To determine the nature of SF-TDDFT states, we checked \( \langle S^2 \rangle \) and the CI coefficients during the optimization. With ROKS, there are two open-shell electrons. These two singly occupied orbitals in the reference triplet state should be HOMO and LUMO in the \( S_0 \) state. Let us denote the electron configuration using \( H \) and \( L \), which correspond to the HOMO and LUMO, and \( a \) and \( b \), which mean \( \alpha \) and \( \beta \) spin, respectively. For instance, the reference triplet state becomes \( HaLa \) in this notation. The \( S_0 \) state should satisfy following two conditions: \( \langle S^2 \rangle \approx 0.0 \) and \( C^2(HaHb) \approx 1.0 \), where \( C \) is a CI coefficient. \( S_1 \) consists mainly of the \( (\text{HOMO})^1(\text{LUMO})^1 \) configurations. Thus, \( C^2(HaHb) + C^2(HbLa) \) is usually around 1.0 for this state. We employed the following scheme for the \( S_1/S_0 \) MECI search using the SMF ADFD approach:

1. Starting from ROKS triplet state, obtain the three lowest states by SF-TDDFT. These three states usually are \( S_0 \), \( S_1 \), and \( T_1 \).

2. Calculate the following \( T \) index value for each state:

\[
T = \langle S^2 \rangle + C^2(\text{HaHb}) + C^2(\text{HaLb}) + C^2(\text{HbLa}) + C^2(\text{LaLa})
\]  

(2)

The \( T \) index should be 3 and 1 for pure \( (\text{HOMO})^1(\text{LUMO})^1 \) triplet and singlet states, respectively, and 1 for pure \( (\text{HOMO})^2 \) and \( (\text{LUMO})^2 \) closed-shell singlet states. This would be 1 for states originating from excitations outside of the \( 2 \times 2 \) \( (\text{HOMO})(\text{LUMO}) \) configuration space; such states are mixtures of singlet and triplet states by the nature of the SF-TDDFT method.

3. Compare three \( T \) values of the lowest three SF-TDDFT states; states with two smaller \( T \) values are judged to correspond to singlet-like states.

4. Calculate the energy gradients for singlet-like states and generate the next geometry for the \( S_1/S_0 \) MECI search. This state selection scheme based on the \( T \) value does not change the wave function and thus does not avoid spin contamination during geometry optimization. However, near the FC geometry and \( S_1/S_0 \) CI, the pure triplet state within the \( 2 \times 2 \) active space is automatically excluded.

After an \( S_1/S_0 \) MECI is obtained, meta-IRC \( C_{1p} \) (mass-weighted steepest descent path) calculation on the \( S_0 \) state from this MECI was performed to check the direct (without barrier) connectivity of MECI to the \( S_0 \) minimum. Geometry optimization on \( S_1 \) from the FC geometry as well as that from each MECI was also performed to check whether the FC and the MECI geometries are connected directly (without barrier) to the \( S_1 \) minimum. The results will be discussed for each system in the Results and Discussion section.

3. RESULTS AND DISCUSSION

3.1. Determination of Critical Points for Molecules 1–3. Molecule 1. Figure 2 shows the structure of important critical points and their energies for molecule 1. Table 2 shows essential geometrical parameters, CC bond distances, and CCCX (X = C, H) dihedral angles of these critical points, and Table 2 gives electronic structure characteristics for these critical points, such as the \( \langle S^2 \rangle \) value, CI coefficients, and \( T \) index.

A local minimum \( LM \) on the \( S_1 \) surface is found near the \( C_3 \), FC point (the ground-state minimum GM) with a planar symmetric \( D_{2h} \) structure, in which the \( C_2 \equiv C_3 \) and weaker \( C_4 \equiv C_5 \) double bond characters of the \( S_0 \) state GM are qualitatively retained, as seen in Table 1. The gradient at FC on \( S_1 \) is sloped to the direction of \( LM \), and the meta-IRC from FC confirms that \( LM \) is reached without barrier. \( LM \) is 97.6 kJ mol\(^{-1}\) lower than \( FC \). The electronic structure characteristics of \( S_1 \) at \( LM \) in Table 2 indicate that this state is somewhat spin-contaminated, but it can still be assigned to a singlet state. Actually, a triplet \( T_1 \) state is relatively close to the \( S_1 \) state at this geometry, which causes spin contamination. However, the shape of the \( S_1 \) and \( T_1 \) PESs would not be much affected by spin mixing.

The optimized MECI \( C_{1p} \) also has a planar symmetric \( D_{2h} \) geometry. Comparing with the geometries of GM and \( LM \), \( C_{1p} \) shows a profound bond alternation; \( C_1 \equiv C_2 \) and the other corresponding bonds became short, and \( C_2 \equiv C_3 \) and \( C_4 \equiv C_5 \) and the other corresponding bonds became long, totally opposite to the bond character of GM and \( LM \). Thus, one can say that this MECI created is due to the bond alternation of the COT ring. The bond alternation lowers the energy of \( S_1 \) and at the same time raises the energy of \( S_0 \), resulting in CIs. \( C_{1p} \) is lower in energy than FC by 85.9 kJ mol\(^{-1}\) and is higher than \( LM \) only by 11.7 kJ mol\(^{-1}\). The meta-IRC calculations from FC and \( C_{1p} \) on the \( S_1 \) surface confirm that both FC and \( C_{1p} \) are connected to \( LM \) downhill on \( S_1 \) without a barrier. The meta-IRC calculation from \( C_{1p} \) on the \( S_0 \) surface also confirms that \( C_{1p} \) is connected to GM on \( S_0 \) without a barrier.

We also found a different type of MECI, \( C_{1p} \), which is 32.0 kJ mol\(^{-1}\) lower than FC. We did not explore the lowest-energy path from FC to \( C_{1p} \). However, TDDFT calculations along optimization steps between \( C_{1p} \) and GM on the \( S_0 \) surface suggest that the barrier between them would not exceed 20.0 kJ mol\(^{-1}\) relative to FC. Therefore, \( C_{1p} \) is less favored than \( C_{1p} \), but it is still reachable on the \( S_1 \) surface starting from the FC energy and geometry. An optimization from \( C_{1p} \) on \( S_0 \) suggests that \( C_{1p} \) is connected to GM on \( S_0 \) without a high barrier.

This \( C_{1p} \) with \( C_1 \) symmetry shows large out-of-plane bending of two neighboring CH bonds in COT. The dihedral angle \( C_5-C_6-C_7-H_d \) is 81.9°, with \( H_d \) almost perpendicular to the COT \( C_5-C_6-C_7 \) plane, and the \( C_8-C_7-C_6-H_c \) and \( C_4-\)
Table 1. Important CC Bond Distances and CCCX (X = C, H) Dihedral Angles at the $S_0$ Global Minimum (FC), $S_1$ Local Minima (LMs), and $S_1/S_0$ MECIs (CIs) of Molecules 1–3

<table>
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<th>molecule</th>
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<th>2</th>
<th>3</th>
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<tr>
<td></td>
<td>FC</td>
<td>LM</td>
<td>CI</td>
</tr>
<tr>
<td>Bond Distance (Å)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>symmetry</td>
<td>C$_{2v}$</td>
<td>D$_{2h}$</td>
<td>D$_{2h}$</td>
</tr>
</tbody>
</table>

Table 2. $\langle S^2 \rangle$, CI Coefficients, and T Index Values for $S_0$ and $S_1$ States at the $S_0$ Global Minimum (FC), $S_1$ Local Minima (LMs), and $S_1/S_0$ MECIs (CIs) of Molecules 1–3

<table>
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<th>molecule</th>
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<th>2</th>
<th>3</th>
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<tbody>
<tr>
<td></td>
<td>FC</td>
<td>LM</td>
<td>CI</td>
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<tr>
<td>$S_0$</td>
<td>0.003</td>
<td>0.005</td>
<td>0.410</td>
</tr>
<tr>
<td>CI(HaHb)</td>
<td>0.999</td>
<td>-0.998</td>
<td>-0.821</td>
</tr>
<tr>
<td>CI(HaLb)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.556</td>
</tr>
<tr>
<td>CI(HbLa)</td>
<td>0.000</td>
<td>0.000</td>
<td>0.079</td>
</tr>
<tr>
<td>CI(HbLb)</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.080</td>
</tr>
<tr>
<td>T index</td>
<td>1.001</td>
<td>1.001</td>
<td>1.405</td>
</tr>
<tr>
<td>$S_1$</td>
<td>0.062</td>
<td>0.088</td>
<td>0.253</td>
</tr>
<tr>
<td>CI(HaHb)</td>
<td>0.578</td>
<td>0.549</td>
<td>0.000</td>
</tr>
<tr>
<td>CI(HaLb)</td>
<td>-0.813</td>
<td>-0.833</td>
<td>0.891</td>
</tr>
<tr>
<td>CI(LaLb)</td>
<td>0.000</td>
<td>0.000</td>
<td>-0.403</td>
</tr>
<tr>
<td>T index</td>
<td>1.057</td>
<td>1.083</td>
<td>1.244</td>
</tr>
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C5–C6–Hc are 37.9 and $-19.2^{\circ}$, respectively, with the Hc very much twist-bent from the COT C5–C6–C7 plane (Table 1). A CI similar to this has been found for COT$^{25}$ and is also similar to the twisted CI of stilbene.$^{20,26}$ As seen in Table 2, at this CI, $S_1$ and $T_1$ are strongly spin-contaminated; $\langle S^2 \rangle$ for the $S_1$ and $T_1$ states is 0.93 and 1.05, respectively (Table 2). The T index for the SF-TDDFT state 2 is smaller than that of state 3, and hence, state 2 is assigned to $S_1$ and state 3 to $T_1$. Because the energy difference between states 2 and 3 is only 28 kJ mol$^{-1}$, the crossing between $S_0$ and the spin-pure $S_1$ state should have a similar geometry to the crossing structure obtained for the heavily spin-mixed state. To examine these states, single-point (4,4) CASSCF calculation is also performed. HOMO$-1$, HOMO, LUMO, and LUMO$+1$ are taken into
active orbitals, and $S_0$ and $S_1$ states are averaged. As shown in Table 3, the $S_0$ state in SF-TDDFT corresponds to the $S_1$ state in CASSCF. On the other hand, $S_1$ and $T_1$ states in SF-TDDFT correspond to linear combinations of $S_0$ and $T_1$ states in CASSCF. This reflects the fault of the SF-TDDFT method; for more quantitative description of these states, a more accurate and contamination-free method such as CASPT2 is needed.

Interestingly, at both $CIF_{\alpha}$ and $CIF_{\beta}$ deformation mainly takes place on the COT ring. In a preliminary calculation with a small basis set, we also found other CIs with out-of-plane CH bending of benzene ring hydrogens. However, these types of CIs have much higher energy and will not contribute to the quenching of luminescence, and therefore, such CIs will not be discussed in the present paper. The reason why the deformation takes place on the COT ring comes from the nature of the excited state. Figure 3 shows two singly occupied orbitals (called HOMO-$\alpha$ and LUMO-$\alpha$) from the ROKS triplet reference calculation at the $S_1$ LM geometry of molecule 1.

orbital distortion is quite different from those of 1, $CIF_{\beta}$ promoted by bond alternation, and $CIF_{\alpha}$ associated with the C–H out-of-plane bending.

Another flat CI, similar to $CIF_{\beta}$ of 1, may also exist. We also tried to find such a CI from LM, but finally we obtained only this pseudo-tub CI. We conclude that such a flat CI in molecule 2 does not exist or is substantially higher in energy. This CI for molecule 2 is lower than the $S_1$ FC by 33.5 kJ mol$^{-1}$ but 57.8 kJ mol$^{-1}$ higher than $S_1$ LM. Although the required energy is not so small, this CI is still accessible from FC. The meta-IRC calculations from FC and CI on the $S_1$ surface confirm that both FC and CI are connected to LM downhill on $S_1$ without a barrier. The meta-IRC calculation from CI on the $S_0$ surface also confirms that CI is connected to GM downhill on $S_0$ without a barrier.

Differing from 1, the pseudo-tub-shaped CI is the only MECI lower than FC. In preliminary calculation with a small basis set, we also found other CIs that have strong CH out-of-plane bending as in $CIF_{\alpha}$ of 1. However, this CI is much higher in energy than FC. Thus, we will not consider these high-energy CIs in the later discussion.

Table 2 indicates that both LM and CI are nearly pure singlet states with small $\langle S^2 \rangle$ values and the $T$ indices of nearly 1. At LM, $S_0$ is a closed shell, and $S_1$ is an open-shell singlet, and at CI, the two singlets are fully mixed.

### Table 3. Energy, $\langle S^2 \rangle$ Value, CI Coefficients, and $T$ Index Values for $T_1$, $S_0$, $S_1$, and $T_2$ States of SF-TDDFT at the $S_1/S_0$ MECI ($CIF_{\alpha}$) of Molecule 1 along with (4,4)-CASSCF Energy and CI Coefficients for $S_0$, $T_1$, and $S_1$ States at the Same Geometry

<table>
<thead>
<tr>
<th>State</th>
<th>SF-TDDFT $T_1$ (ROKS state)</th>
<th>SF-TDDFT $S_0$</th>
<th>SF-TDDFT $S_1$</th>
<th>SF-TDDFT $T_1$</th>
<th>2SA (4,4)-CASSCF $S_0$</th>
<th>2SA (4,4)-CASSCF $T_1$</th>
<th>2SA (4,4)-CASSCF $S_1$</th>
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<tr>
<td>$\Delta E$ (kJ/mol)</td>
<td>0.0</td>
<td>30.5</td>
<td>30.5</td>
<td>58.4</td>
<td>0.0</td>
<td>26.0</td>
<td>60.1</td>
</tr>
<tr>
<td>$\langle S^2 \rangle$</td>
<td>2</td>
<td>0.1482</td>
<td>0.9301</td>
<td>1.0531</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>CI(HaHb)</td>
<td>0.0000</td>
<td>-0.9180</td>
<td>-0.1043</td>
<td>0.1132</td>
<td>-0.0769</td>
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<td>0.9046</td>
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<tr>
<td>CI(HaLb)</td>
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<tr>
<td>CI(LaLb)</td>
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<tr>
<td>$T$ index</td>
<td>1.056</td>
<td>1.906</td>
<td>1.996</td>
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<td></td>
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</table>

Figure 4. Potential energy profile of molecule 2. Solid lines mean that connections between points are confirmed by meta-IRC or geometry optimization. Connections with dotted lines are not confirmed.

Figure 5. Schematic representation of critical points of molecule 2.
Molecule 3. There is a noticeable difference between molecule 3 and molecules 1 and 2. For molecule 3, two C\textsubscript{2v} local minima for S\textsubscript{1} state were found (Figure 6 and Table 2). As found previously\textsuperscript{3}, there is one local minimum LM\textsubscript{v} that has a shallow V shape and another local minimum LM\textsubscript{f} with flat C\textsubscript{2v} geometry. LM\textsubscript{v} is lower in energy by 12.5 kJ mol\textsuperscript{-1} than LM\textsubscript{f}. This is different from a previous study, in which relaxed scan found LM\textsubscript{f} slightly lower than LM\textsubscript{v}. Because the differences between two geometries are as small as the typical error of TD-DFT (around 0.1 eV, namely, 10 kJ mol\textsuperscript{-1}),\textsuperscript{27} we will not discuss this difference further.

At the FC C\textsubscript{2v} V-shaped structure, the lowest singlet excited state S\textsubscript{1} is \textsuperscript{1}A\textsubscript{2}. Following the meta-IRC from FC, LM\textsubscript{f} still with a V-shaped structure with a smaller bending angle, is reached with \textsuperscript{1}A\textsubscript{2} as S\textsubscript{1}. As the molecule become even more planar, \textsuperscript{1}B\textsubscript{2} becomes lower than \textsuperscript{1}A\textsubscript{2}. At the second S\textsubscript{1} minimum LM\textsubscript{f}, the molecule is coplanar, and the first excited state is \textsuperscript{1}B\textsubscript{2}. The electronic transition (emission) from \textsuperscript{1}B\textsubscript{2} to S\textsubscript{0} (\textsuperscript{1}A\textsubscript{1}) is allowed, while that from \textsuperscript{1}A\textsubscript{2} to S\textsubscript{0} is forbidden. Thus, molecule 3 can give emission from the second S\textsubscript{1} minimum LM\textsubscript{v} but not from the first minimum LM\textsubscript{f}. The calculated vertical emission energy (without zero-point energy correction) from LM\textsubscript{v} is 179 kJ mol\textsuperscript{-1}, while that of experiment in solution is 230 kJ mol\textsuperscript{-1} (520 nm).

Between the two minima LM\textsubscript{v} and LM\textsubscript{f}, there should be a transition state due to avoided crossing of the two electronic states. It is not easy to describe this avoided crossing with the SF-TDDFT method, and a search based on SF-TDDFT did not give a reliable TS structure. However, from an approximate scan of the two states, one can say that the barrier between LM\textsubscript{v} and LM\textsubscript{f} would be less than 20 kJ mol\textsuperscript{-1}. The process going from FC though LM\textsubscript{v} to LM\textsubscript{f} would be a viable step.

In molecule 3, the COT moiety is aplanar in the ground state. Thus, conjugation is divided into two parts. On the other hand, at the LM\textsubscript{f}, the COT moiety becomes planar, and conjugation becomes enlarged to the whole system. This delocalization stabilizes the \textsuperscript{1}B\textsubscript{2} state, and the order of excited states is switched.

One MECI, labeled CI, has been found for molecule 3. CI is higher in energy than the FC structure FC by 56.3 kJ mol\textsuperscript{-1}. This structure CI consists of nearly two planar acene structures that are connected by a nearly perpendicularly twisted COT structure, similar to the CI structure of 2. A flat CI like 1 could not be found, which is the same result as 2. It is interesting to follow the structure change of molecule 3 on S\textsubscript{1}: deeply V-shaped FC, followed by shallowly V-shaped LM\textsubscript{v}, coplanar LM\textsubscript{f}, and twisted CI.

One notices that CI of molecule 2 is lower than FC by 33.5 kJ mol\textsuperscript{-1}, while CI of molecule 3 is higher than FC by 56.3 kJ mol\textsuperscript{-1}. As shown in Table 1, structures of CI for 2 and 3 are similar. Thus, it is difficult to explain this energy difference from a structural point of view. To verify electronic structure at CIs, we performed S\textsubscript{0}/S\textsubscript{1} state-average (4,4) CASSCF/6-31+(d) single-point calculation at the MECI CI for both molecule 2 and 3. In Figure 7, four natural orbitals (NOs) of 2 and 3 are shown (isovales = 0.025). Apparently, their orbitals are very similar, and the natural orbital occupation numbers (NOONs) are also similar. For molecule 2, the NOON for each NO for state 1 is 1.882, 1.405, 0.612, and 0.100, respectively; for molecule 3, the NOON for each NO is 1.799, 1.329, 0.705, and 0.167, respectively. We can conclude that the difference between electronic structures on CI for 2 and 3 is not large enough to explain energetics on CI.

One significant difference, as shown in Figure 8, between 2 and 3 is the symmetry of LMs. As shown in Table 1, LM for 2 is a rectangle belonging to D\textsubscript{2h}, while LM for 3 loses C\textsubscript{2v} symmetry around the z-axis and is a trapezoid belonging to C\textsubscript{2v}. On the other hand, the CIs for both 2 and 3 are a twisted rectangle, possessing C\textsubscript{2v} rotational symmetry around the z-axis. Now, we introduce for 3 a hypothetical D\textsubscript{2h} structure H\textsubscript{D2h} by symmetrizing the LM, C\textsubscript{2v} structure. The energy difference between CI and LM can now be rewritten as

Figure 6. Potential energy profile of molecule 3. Solid lines mean that connections between points are confirmed by meta-IRC or geometry optimization. Connections with dotted lines are not confirmed.

Figure 7. (a) Two-state SA (4,4) CASSCF NOs at CI for molecule 2. The occupation number for each NO for state 1 is 1.882, 1.405, 0.612, and 0.100, respectively. (b) Two-state SA (4,4) CASSCF NOs at CI for molecule 3. The occupation number for each NO is 1.799, 1.329, 0.705, and 0.167, respectively.
In molecule 1, the pathway toward CI_R from FC is not on the steepest descent path and should be accessible from FC with some activation energy. This path not on the minimum-energy pathway may contribute but is not likely to compete against the steepest descent quenching path via MECI CI_F in the gas phase or in solution.

In solid, however, large structural changes should be inhibited by the surroundings. Thus, CI_F that requires a large geometry change from the FC V structure to a planar structure may not be reachable. However, CI_R is lower in energy than FC and requires relatively small structural change (a CH out-of-plane bending retaining the V-shape structure). Thus, CI_R is expected to be reachable even in the solid state. Therefore, we propose that the quenching of molecule 1 via CI_R is still possible in solid, explaining qualitatively the experimental finding of no emission either in solution or in solid for molecule 1.

On the other hand, in molecule 2, there is only one type of MECI, CI, with lower energy in the vicinity of FC. No CI for 2, similar to CI_R in molecule 1, could not be located in the GRRM SMF search, suggesting that this, if it exists, is substantially higher in energy than FC. The electronic transition (emission) from S_1 to S_0 is forbidden by symmetry and should be weak. The molecule 2 moves easily to the MECI CI, through which the molecule moves on to the S_0 ground state to reach the S_0 ground minimum, as in molecule 1. This should be the favorable quenching pathway in the gas phase and in solution. As discussed for molecule 1, this pathway of quenching would be prohibitive in solid also for molecule 2. This pathway from the V-shape FC through coplanar LM to twisted CI requires a large geometrical change and will be inhibited by surroundings.

The above argument qualitatively explains why molecule 2 is nonemissive in solution and is only weakly emissive in solid.

In molecule 3, the situation is totally different from 1 and 2. At LM_F, the transition between S_1 and S_0 is allowed by symmetry. In addition, the barrier toward CI is high enough. Thus, in this molecule, fluorescence is more likely to take place than internal conversion in either the solution or solid, consistent with experimental observations.

4. CONCLUSION

We have explored quenching pathways of three multi-luminescent molecules using SF-TDDFT in conjunction with the GRRM ADDF automatic search method for MECI and proposed different quenching mechanisms for three different molecules 1, 2, and 3. As a referee suggested, it may be hard to believe that the photochemistry of these structurally similar molecules is qualitatively as different as reported. A standard search from a guess would have missed this difference. The unbiased and global search of MECIs by the GRRM ADDF method demonstrated that dramatic change in MECI characteristics and emission behavior is exactly what is taking place going from molecule 1 to 2 to 3.

Molecule 1 with phenyleneimide has two low-energy MECIs, CI_L and CI_R. In contrast to the strongly V-shaped FC structure, CI_L has a flat structure and is lower than FC by 86 kJ mol^{-1} and is connected via the local minimum LM (12 kJ mol^{-1} lower than CI_L) to FC directly without barrier. Thus, the excited molecule should be quenched very easily in the gas phase and in solution in which a large geometrical distortion from FC to CI_L can be accomplished. The other CI_CI_R is energetically less favorable than CI_L and is not likely to compete against the quenching from CI_L. However, this CI involves only CH out-of...
of-plane motion that requires smaller geometry changes than the flat CI. Thus, CI can be reached even in solid and provides the quenching pathway in solid.

Molecule 2 with naphthaleneimide has only one conical intersection CI in the region that is lower in energy than the FC state. This CI shows a twisted structure with acene wings on the side of the tub-shaped cyclo-octatetraene ring and requires a large molecular motion. Thus, this CI is the quenching pathway in the gas phase and solution. However, in solid, this CI cannot be reached, and molecule 2 should be able to stay in the excited state and emit.

Different from the two molecules above, molecule 3 with anthraceneimide has no CI that is lower in energy than the FC state. Therefore, the quenching is not available in solution as well as in solid. Moreover, at the equilibrium structure in the S1 state, transition from S1 to S0 is allowed by symmetry. Thus, this molecule is emissive even in solution.

We can conclude that the difference of emission behavior is determined by the difference of structures and energies of CIs. We succeeded in qualitatively explaining different emission behavior of three multiluminescent molecules. The present method of determining the structures and energies of low-energy CI using the GRRM strategy should be applicable to other photofunctional molecules, and such studies are in progress. Nonadiabatic molecular dynamics is required to quantitatively reproduce experimental results.

■ ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b07682.

Cartesian coordinates of all the optimized structures (PDF)

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### Notes

The authors declare no competing financial interest.

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### REFERENCES


