Density Functional Studies on Photophysical Properties of Boron-Pyridyl-Imino-Isoindoline Dyes: Effect of the Fusion

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ABSTRACT: In this work, to make out the aryl-fusion effect on the photophysical properties of boron-pyridyl-imino-isouindoline dyes, compounds 1-5 were theoretically studied through analyses of their geometric and electronic structures, optical properties, transport abilities, and radiative (k_r) and non-radiative decay rate (k_nr) constants. The highest occupied molecular orbitals of aryl-fused compounds 2-5 are higher owing to the extended conjugation. Interestingly, aryl fusion in pyridyl increases the lowest unoccupied molecular orbital (LUMO) level, while isouindoline decreases the LUMO level; thus, 4 and 5 with aryl fusion both in pyridyl and isouindoline exhibit a similar LUMO to 1. Compounds 4 and 5 show relatively low ionization potentials and high electron affinities, suggesting a better ability to inject holes and electrons. Importantly, the aryl fusion is conducive to the decrease of k_nr. The designed compound 5 exhibits a red-shifted emission maximum, low k_r, and low k_nr, which endow it with great potential for applications in organic electronics. Our investigation provides an in-depth understanding of the aryl-fusion effect on boron-pyridyl-imino-isouindoline dyes at molecular levels and demonstrates that it is achievable.

INTRODUCTION

Organic fluorescent dyes have been continually developed, which is motivated by their application in biomedical analysis, fluorescence labeling, organic light-emitting diodes (OLEDs), and organic photovoltaic devices. Many diverse types of fluorescent dyes have been investigated and developed based on polyaromatics, coumarin, porphyrins, cyanines, etc. In these issues, the incorporation of the boron element into the conjugated systems is one of the valid strategies for constructing a luminescent building block, which can be employed to generate a wide variety of fluorescent dyes. The unique electronic properties of organic conjugated boron dyes that stem from p–π interactions between the empty p orbital of boron and π-conjugation systems continue to fascinate researchers. Herein, tetracoordinate boron complexes have been demonstrated to be effective luminescent materials for various applications ranging from materials science to biology and medicine. Their electronic and spectroscopic properties can be readily tuned by synthetically introducing suitable substituents or altering ligands. Among them, boron dipyrromethene (BODIPY) is the most commonly employed. The ligand framework of the BODIPY core, which has constructed a variety of fluorescent dyes including single and multiple boron centers, provides a versatile scaffold for chemical modification. Many researchers have studied and developed various BODIPY-based sensitizers/emitters and demonstrated the potential of BODIPYs for applications in OLEDs, organic semiconductors, and dye-sensitized solar cells.

Despite the wide research and applications of available BODIPY fluorophores, further investigation into the derivatization of BODIPYs has remained active. Much effort has been devoted to the chemical modification of the BODIPY core, such as incorporation of heteroatoms (aza-BODIPY derivatives), which might pave the way for generating novel fluorescent dyes with desired properties and developing efficient optoelectronic devices. Desymmetrization of the BODIPY core structure, an efficient strategy for structural modification operation, has been employed to regulate properties, and consequently many versatile boron-based dyes were successfully prepared. For example, Thompson and co-workers reported some BODIPY derivatives by replacing the pyrroles in BODIPY with pyridine moieties, and these monomers and homoleptic meso-linked dimers are found to be highly promising...
for application to optoelectronic technologies.  

Maeda et al. synthesized several BODIPY dyes based on the carbazole skeleton, which exhibit large Stokes shifts and color-tunable solid-state fluorescence. In 2014, Liu et al. reported a series of asymmetric BODIPY analogues, boron-pyridyl-imino-isoindoline dyes, which show high fluorescence quantum yields in solution as well as in the solid state (1−4 are depicted in Figure 1). Compared to 1, compounds 2, 4, and 5 have aryl fusion in the pyridyl substructure, while 3−5 have aryl fusion in the isoindoline portion. However, their spectra properties and quantum yields are greatly different, which are clearly in connection with the location and extent of the fused aryl. A better understanding of fluorophores has dramatic implications for tailoring the properties of boron-based dyes. Herein, we investigate the reported compounds 1−4 using the density functional theory (DFT) method to provide insight into the aryl-fusion effect on the photophysical properties and to understand the structure−property relationships since quantum chemical calculations have been considered to be an important and low-cost avenue in revealing the origin of photophysical properties and assisting molecular design. From our investigations, it was proposed that the incorporation of aryl into isoindoline and pyridyl moieties of boron dyes could play a critical role in decreasing the non-radiative decay rate constants ($k_{nr}$). Furthermore, compound 5 was designed with the aim of obtaining an efficient and versatile fluorescent dye for optoelectronics. Our calculated results show that 5 has a red-shifted emission wavelength, low $\lambda_{\text{fl}}$ and high $k_{\text{r}}$ and low $k_{\text{IC}}$.

## RESULTS AND DISCUSSION

**Geometrical and Electronic Structures.** The geometrical structures of 1−5 were first investigated since they can directly impact the electronic and spectral properties. The selected geometrical parameters optimized at the PCM-B3LYP/6-31+G(d,p) level in solution together with the available X-ray crystal diffraction data are collected in Table S1 (in the Supporting information). All five compounds show a significantly planar skeleton, which will facilitate extension of the $\pi$ conjugation. The bond lengths in the isoindoline substructure of 3−5, which have aryl fusion, are significantly different from those of 1 and 2, suggesting the great influence of the incorporation of aryl into the isoindoline substructure. The bond lengths in the pyridyl part of 2 and 4 are also different from those of 1, indicating that aryl fusion in the pyridyl portion has a direct impact on geometric configurations. Importantly, 5 shows very different bond length variations from 1−4 in pyridyl from which the different properties can be predicted. The geometric variations of the five compounds suggest that the isoindoline and pyridyl portion of boron-pyridyl-imino-isoindoline dyes are sensitively influenced by aryl fusion, which may drastically change the electronic and spectroscopic properties.

The comparison of the frontier molecular orbitals among the five compounds allows a qualitative analysis of the aryl-fusion effect; thus, the plots of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), energy levels, and the energy gaps for 1−5 at their optimized $S_0$ geometries are illustrated in Figure 2. The BF$_2$

![Figure 1](https://dx.doi.org/10.1021/acsomega.0c02669)

**Figure 1.** The studied molecular structures of 1−5.

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c02669)

**Figure 2.** Frontier orbital plots, HOMO and LUMO energy levels, and energy gaps for 1−5 at their ground state obtained at the PCM-B3LYP/6-31+G(d,p) level.

moiety makes a negligible contribution to the frontier orbitals of the five compounds. The HOMOs and LUMOs of 1−5 mainly distribute on the $\pi$-conjugated skeleton and are generally delocalized. Compound 2 has slightly more contribution from pyridyl and the fused benzene in HOMO, while 3 and 4 have slightly more contribution from isoindole and the fused moiety, which is directly related to the fusion of the aryl into the pyridyl and isoindoline moieties. As shown in Figure 2, the HOMOs of 2−5 are higher than that of 1 owing to the extended conjugation, indicating that the electronic properties are significantly affected by aryl fusion in the pyridyl and isoindoline moiety. Interestingly, the LUMO of 2, which has aryl fusion in 21068
pyridyl, is decreased compared to that of 1, while the LUMO of 3, which has aryl fusion in isooindoline, is increased. Compounds 4 and 5 with aryl fusion in both pyridyl and isooindoline have comparable LUMO levels to compound 1. This strategy of keeping the LUMO unchanged and regulating HOMO individually plays an important role in shaping excited-state properties and defining the electronic and optical properties of conjugated dyes. From the above discussion, it can be seen that the aryl fusion of the isooindoline and pyridyl moiety is favorable for ready manipulation of the electronic structure; thus, differently different photophysical properties can be expected.

**Optical Properties.** To inspect the electronic transition properties of 1–5, the absorption and emission spectra have been calculated at the PCM(CH2Cl2)-TD-TPSSH/6-311+g-(2d,p) level based on optimized geometrical configurations. The excitation energies of BODIPY and aza-BODIPY dyes are usually overestimated through TD-DFT methods. Recently, several published works of Jacquemin et al. and Brown et al. tried to provide accurate theoretical estimates and to address the systematic shift of TD-DFT results. However, the calculation of the excited-state properties of BODIPY and aza-BODIPY dyes is still a great challenge for quantum mechanical methods. To achieve more accurate results, taking 1 as an example, some representative functionals including B3PW91, B3LYP, BHandHLYP, BMK, CAM-B3LYP, HSEh1PBE, M06, PBE0, HCTHlyp, TPSSH, and ωB97D have been tested. The calculated results and the corresponding experimental data are illustrated in Figure S1, which suggest that TPSSH provides the most reasonable results; thus, TPSSH was adopted for the calculation of absorption and emission spectra for 1–5. Combining the distribution of frontier orbital plots in Figure 2 with the nature of absorption data in Table 1, π → π* electronic transitions in compounds 1–5 are always observed. The absorption maxima of 1–5 are related to the S0 → S1 transition mainly described by the excitation from the HOMO to the LUMO. The absorption peaks of 2–5 show a clear red shift compared with that of 1, which is consistent with the tendency of the energy gaps discussed above. For emission spectra, the maximum absorption peaks of 1–5 correspond to S1 → S0 transition and mainly contributed by the electronic transitions of LUMO → HOMO. In Table 2, the results of 0–0 energies (λem) are also listed. It can be seen that the results of 0–0 show a blue shift as compared to those of the vertical emission wavelength (λem) and the values of Stokes shift between λem and λ0, of 1–4 are in good agreement with experimental data. Additionally, many works have been devoted to improving the calculation accuracy of BODIPY dyes. For example, double-hybrid density functionals evaluated by Grimme and coworkers show high robustness and accuracy. Jacquemin and coworkers have shown that the hybrid (SOS)-CIS(D) method and wave function-based Bethe–Salpeter approach could provide reliable excited-state properties for BODIPY dyes. Thus, this interesting and challenging work for the improvement of excitation energies for BODIPY dyes will be further studied in our future work.

**Charge Injection/Transport Abilities.** The charge injection and transport abilities are important considerations in selective organic dyes for optoelectronic devices. In general, lower IP and higher EA will facilitate the injection of holes and electrons from the hole/electron transport layer to the emitter layer. According to Marcus theory, the smaller reorganization energy will induce the greater charge transfer rate. Furthermore, the comparable reorganization energy for electrons (ΔrH) and holes (ΔrL) is beneficial to achieving charge balance and further to enhancing exciton production in the emitter. Charge balance in OLEDs has been shown to be favorable for reducing driving voltage and increasing electroluminescence efficiency and luminous efficiency as well as fabricating single-layer devices. From the calculated data of vertical and adiabatic IP and vertical and adiabatic EA of 1–5 (collected in Table 3), the IP, of 2–5 are much lower than that of 1, indicating a better ability to inject holes. Compared to 1, the EA, values of 2, 4, and 5 are higher, suggesting the ability to inject electrons from the electron transport layer/host material to the emitter is greater. Generally, the increased HOMO/LUMO will lead to the ability to inject electrons from the electron transport layer/host material to the emitter is greater.

### Table 1. Absorption Data for Compounds 1–5 Calculated by PCM(CH2Cl2)-B3LYP/6-31+G(d,p)//PCM(CH2Cl2)-TPSSH/6-311+G(2d,p) Level

| compound | transition | λabs | Ee | f | composition | λem | λexp |
|----------|------------|------|----|---|--------------|----|-----|
| 1        | S0 → S1    | 359.55 | 3.448 | 0.612 | H → L (93%) | 379 |
| 2        | S0 → S1    | 394.49 | 3.143 | 0.394 | H → L (82%) | 406 |
| 3        | S0 → S1    | 415.20 | 2.986 | 0.486 | H → L (96%) | 396 |
| 4        | S0 → S1    | 439.99 | 2.818 | 0.631 | H → L (98%) | 419 |
| 5        | S0 → S1    | 450.72 | 2.752 | 0.676 | H → L (98%) | 419 |

“H” denotes HOMO, and “L” denotes LUMO. Measured in CH2Cl2 solution.

### Table 2. Vertical Emission Wavelength (λem/nm), 0–0 Emission Wavelength (λ0-0/nm), and Stokes Shift (SS/nm) between λ0-0 and λem for 1–5 Calculated by PCM(CH2Cl2)-TD-B3LYP/6-31+G(d,p)//PCM(CH2Cl2)-TPSSH/6-311+G(2d,p) Level

| compound | transition | λem | Ee | f | composition | λ0-0 | SS |
|----------|------------|------|----|---|--------------|------|----|
| 1        | S1 → S0    | 422.97 | 2.931 | 0.644 | L → H (98%) | 390.92 | 31.37 |
| 2        | S1 → S0    | 479.39 | 2.586 | 0.380 | L → H (92%) | 424.66 | 30.17 |
| 3        | S1 → S0    | 454.03 | 2.731 | 0.536 | L → H (96%) | 426.85 | 11.65 |
| 4        | S1 → S0    | 476.16 | 2.604 | 0.706 | L → H (98%) | 448.46 | 8.47 |
| 5        | S1 → S0    | 512.02 | 2.422 | 0.703 | L → H (98%) | 468.81 | 18.32 |

“H” denotes HOMO, and “L” denotes LUMO. Measured in CH2Cl2 solution.
EA. Note that the designed compound 5 has the lowest IP, (6.508 eV) and the highest EA, (3.172 eV), demonstrating a better ability to inject holes and electrons. From the computed data of \( \lambda_h \) and \( \lambda_e \), the values of \( \lambda_h \) and \( \lambda_e \) of aryl-fused compounds 2–5 are much smaller compared to those of 1, and this fact strongly demonstrates the improved carrier transport abilities of 2–5. Additionally, the difference between \( \lambda_h \) and \( \lambda_e \) of 2 (less than 0.040 eV) is much lower, which will be beneficial to achieving balance in carrier transport. The values of \( \lambda_h \) for 3–5 are much lower than those of \( \lambda_e \), suggesting great electron transporting abilities.

**Radiative and Non-radiative Decay Rate Constants.**

The radiative decay rate \( k_r \) and non-radiative decay rate \( k_n \) from S1 to S0 in CH2Cl2 solution are computed, and the results are listed in Table 4. For the non-radiative decay, only the internal conversion decay rates \( k_{IC} \) were analyzed since the intersystem crossing (IC) process of flexible molecules cannot compete with \( k_r \) and \( k_{IC} \). The IC decay is closely related to the geometric distortions between the S1 and S0 states and can be measured by reorganization energy, which has been proven to be a helpful parameter to determine the geometric relaxation. From the results illustrated in Figure 3, it is clearly seen that the normal modes with relatively large reorganization energies are mainly located in the high-frequency region (more than 1100 cm\(^{-1}\)) for 1–5. The largest reorganization energy comes from the in-plane motion, such as the stretching vibration of C–N and C=O, and the bending vibration of C–H. It can be seen that there is one representative normal mode with large reorganization energy (>300 cm\(^{-1}\)) for 1 and two with large reorganization energy for 2, while all the normal modes of 3–5 have relatively small reorganization energy (<250 cm\(^{-1}\)). The Huang–Rhyls (HR) factor is another helpful parameter to characterize the excited-state energy consumption through the non-radiative decay channel. From the calculated results of HR factors (shown in Figure 4 and the insets), the large values of HR factors of 1, such as 0.20 (379.53 cm\(^{-1}\)) and 0.47 (1479.08 cm\(^{-1}\)), mainly correspond to stretching vibrations of C–N and bending motions of C–H. There are three normal modes with a large HR factor for 2, 0.23 (192.72 cm\(^{-1}\)), 0.28 (504.20 cm\(^{-1}\)), and 0.39 (1475.28 cm\(^{-1}\)), which also correspond to in-plane motions. For compounds 3–5, all the HR factors are less than 0.2. The presented results reveal that the S1 state of 1 and 2 undergoes larger geometric relaxation since they show relatively larger reorganization energies and HR factors.

Importantly, \( k_{IC} \) and \( k_{r} \) of 1–5 were computed and the results are collected in Table 4. The \( k_r \) of compounds 1–5 (2.34 \( \times \) 10\(^8\), 1.86 \( \times \) 10\(^8\), 2.24 \( \times \) 10\(^8\), 2.67 \( \times \) 10\(^8\), and 2.21 \( \times \) 10\(^8\), respectively) are comparative, and only that of 2 is relatively lower. From the previous works, \( k_r \) is closely connected with the electric transition dipole moment (\( \mu \)) and adiabatic excitation energy (\( E_\text{ad} \)). The small \( \mu \) (8.550 D) of 2 leads to the lower \( k_r \), while the values of \( \mu \) for compounds 1 and 3–5 are clearly large; thus, the data of \( k_r \) are enhanced. The \( k_{IC} \) of 1–5 is 6.69 \( \times \) 10\(^8\), 3.01 \( \times \) 10\(^8\), 1.47 \( \times \) 10\(^8\), 2.37 \( \times \) 10\(^8\), and 1.59 \( \times \) 10\(^8\) s\(^{-1}\), respectively. 1 has the largest \( k_{IC} \) owing to the relatively strong geometric relaxation in S1; therefore, the fluorescence quantum yield of 1 is low, which is in line with experimental results. Importantly, the results of \( k_{IC} \) for 2–4 are greatly reduced; thus, they show high fluorescence quantum yields. It is noticeable that the designed 5 has a high \( k_r \) and a low \( k_{IC} \). Therefore, with one more fused aryl in the pyridyl side, which results in the delocalized frontier orbitals, compound 5 greatly facilitates radiative transition. This fact may render it a potential alternative to fluorescence dyes in the optoelectronics field.

### CONCLUSIONS

In this work, the photophysical properties of compounds 1–5 were thoroughly investigated. The calculated results reveal that incorporating aryl into isoinodoline and pyridyl substructures directly impacts the geometric and electronic structures, transporting properties, and fluorescence efficiencies. The results show that aryl fusion in different sites will affect the frontier orbital level. Aryl fusion in pyridyl will increase the LUMO level (compound 2), while aryl fusion in isoinodoline will decrease the LUMO level (compound 3). 4 and 5 with aryl fusion both in pyridyl and isoinodoline exhibit nearly unchanged LUMOs. The aryl-fused compounds 2–5 show relatively low IP and high EA, suggesting their better ability to inject holes and electrons. Compound 2 has comparable \( \lambda_h \) and \( \lambda_e \) which will be favorable for achieving better balance in carrier transport. The computed results of \( k_r \) and \( k_{IC} \) show that the aryl fusion is conducive to the decrease of the \( k_{IC} \); thus, the fluorescence efficiencies of 2–5 are greatly enhanced. Importantly, the designed compound 5 shows a red-shifted emission maximum, low \( \lambda_{ad} \) and high \( k_r \) and low \( k_{IC} \) which endow it with great potential for applications in organic electronics.

**Table 3. Calculated Data of Vertical Excitation Energies (\( E_v / eV \)), Adiabatic Excitation Energies (\( E_{ad} / eV \)), Electric Transition Dipole Moments (\( \mu / D \)), Radiative Rates (\( k_r S^{-1} \)), Internal Conversion Rates (\( k_{IC} S^{-1} \)) from S1 to S0 for Compounds 1–5, and Their Reported Experimental Fluorescence Quantum Yields (\( \Phi_{exp} \)).**

| compound | \( E_v \) | \( E_{ad} \) | \( \mu \) | \( k_r \) | \( k_{IC} \) | \( \Phi_{exp}^a \) | \( k_{exp}^b \) | \( k_{r,exp}^b \) |
|----------|-------|--------|------|-----|-----|--------|-----|--------|
| 1        | 2.879 | 3.172  | 8.761| 2.34 \times 10\(^8\) | 6.69 \times 10\(^8\) | 0.33 | 3.3 \times 10\(^8\) | 6.6 \times 10\(^8\) |
| 2        | 2.623 | 2.920  | 8.550| 1.86 \times 10\(^8\) | 3.01 \times 10\(^8\) | 0.74 | 2.9 \times 10\(^8\) | 1.0 \times 10\(^8\) |
| 3        | 2.759 | 2.905  | 8.884| 2.24 \times 10\(^8\) | 1.47 \times 10\(^8\) | 0.86 | 3.8 \times 10\(^8\) | 6.2 \times 10\(^7\) |
| 4        | 2.637 | 2.765  | 10.247| 2.67 \times 10\(^8\) | 2.37 \times 10\(^8\) | 0.93 | 4.8 \times 10\(^8\) | 3.6 \times 10\(^7\) |
| 5        | 2.445 | 2.645  | 10.370| 2.21 \times 10\(^8\) | 1.59 \times 10\(^8\) |

\(^a \) Measured in CH2Cl2 solution. \(^b k_{exp} = \Phi_{exp} / \tau; k_{r,exp} = (1 - \Phi_{exp}) / \tau\)

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All calculations were performed using the Gaussian 09 package, unless otherwise stated. In recent years, density functional theory (DFT) has been considered to be a low-cost and versatile approach to investigate the electronic structures and the hybrid exchange functional B3LYP has been demonstrated to be significantly reliable for computing geometries and vibrational frequencies in organic molecular systems. The ground-state geometries ($S_0$) of 1–5 were fully optimized using the B3LYP/6-31G+(d,p) level within the non-equilibrium polarizable continuum model (PCM) approach to simulate the solvent effects ($\text{CH}_2\text{Cl}_2$). The geometries of the first singlet excited state ($S_1$) were optimized at the PCM-B3LYP/6-31G+(d,p) level using time-dependent DFT (TD-DFT) based on the optimized $S_0$ geometries. Vibrational frequency analysis was carried out to identify the real minima.
The absorption and emission spectra were systematically calculated by the TD-DFT method in solution (CH2Cl2). Symmetry constraints were not applied during all of the calculations. In addition, the comparative molecular geometrical calculations obtained from three representative hybrid functionals (B3LYP, PBE0, B3PW91; see Table S2) have been carried out for compound 1. Evidently, all three functional results can reproduce the experimental values. The S0 geometries optimized using B3LYP match the reported crystal structure and the results are close to those calculated by the functionals PBE0 and B3PW91, which are commonly used for organic small molecules, certifying the reliability of the chosen functional. Moreover, a systematic comparison between the S0 geometries for 1, 2, and 4 optimized at the PCM-B3LYP/6-31+G(d,p) level in CH2Cl2 and the available X-ray crystal diffraction data was performed (Table S3). The MAD between calculated bond lengths of 1, 2, and 4 and corresponding experimental data is no more than 0.014, 0.011, and 0.009 Å, and the maximum error is less than 0.026, 0.017, and 0.019 Å, respectively. The MAD of bond angles for the maximum error is less than 0.026, 0.017, and 0.019 Å, experimental data is no more than 0.014, 0.011, and 0.009 Å, and respectively, indicating the adopted calculation methods can provide reliable results for the investigated compounds. Finally, the comparative λμ calculation obtained from PCM and PCM with state-specific corrections was performed (Table S4) since state-specific corrections may influence the spectra results of asymmetric systems. The results clearly show a slight difference between the PCM and PCM state-specific corrections, and the results with PCM are closer to the experimental value. Thus, only the spectra results with the PCM approach are presented and discussed in this work. The ionization potential (IP), electron affinities (EAs), and internal reorganization energies for holes (λh) and electrons (λe) of 1–5 have been calculated at the PCM-B3LYP/6-31+G(d,p) level to evaluate their transport properties.

The radiative decay rate constant (k) can be calculated by the integration of the light emission spectrum

\[
\sigma_{em}(\omega, T) = \frac{4\omega}{3\hbar c^3} \sum_{uv} P_u(T) \left| \langle \Theta_u | \mu | \Theta_v \rangle \right|^2 \delta(\omega_{uv} - \omega) \tag{1}
\]

where \( \omega \) is the frequency; \( P_u(T) \) is the Boltzmann distribution function of the initial vibronic manifold; \( T \) is the temperature; \( \mu \rightarrow \nu = \langle \Phi \mu | \mu | \Phi \nu \rangle \) is the electric transition dipole moment between the initial (i) and final states (f); and \( \Theta \) is the vibrational wave function.

Based on the Fermi golden rule and Franck–Condon principle, the non-radiative internal conversion decay rate constant (kic) can be calculated as

\[
k_{ic} = \frac{1}{\hbar} \sum_{kl} \int_{-\infty}^{\infty} dt \left( e^{i \omega |t|} e^{-1} \rho_{ic}(t, T) \right) \tag{3}
\]

\[
R_{kl} = \langle \Phi \mu | \mu | \Phi \nu \rangle \langle \Phi \kappa | \kappa | \Phi l \rangle \tag{4}
\]

\[
\rho_{ic,kl}(t, T) = Tr \left( \hat{P}_k e^{i\omega t} \hat{P}_l e^{-i\omega t} \hat{T} \right) \tag{5}
\]

where \( R_{kl} \) is the non-adiabatic electronic coupling, \( \rho_{ic}(t, T) \) is the thermal vibration correlation function (TVCF). The \( k \) and non-radiative decay rate from \( S_i \) to \( S_0 \) in the \( \text{CH}_2\text{Cl}_2 \) solution are computed through the MOMAP package, which shows superiority in the description and prediction of the fluorescence properties of the polyatomic molecules. In the computation of transition constants, the Duschinsky rotation effect was considered by employing the TVCF method, and the Herzberg–Teller effect was not adopted since the studied compounds are relatively rigid.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02669.

Calculated geometric parameters of the five compounds in the ground state in \( \text{CH}_2\text{Cl}_2 \) solution, functional test results, and comparative calculation results obtained from PCM and PCM with state-specific corrections (PDF)

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Notes
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