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Ab initio and first principles theoretical investigations of triplet–triplet fluorescence in trimethylenemethane biradicals†

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Theoretical studies on triplet–triplet ($T_1 \rightarrow T_0$) fluorescence of the arylated trimethylenemethane (TMM) biradicals, $^3\mathbf{2}^{\cdot\cdot}$, were carried out using post-Hartree–Fock *ab initio* and various first principles density functional theory methods. Analysis of optimized geometries including bond alternations and spin distributions indicates that the triplet ground ($^3\mathbf{2}^{\cdot\cdot}$) and excited ($^3\mathbf{2}^{\cdot\cdot}*$) states of these biradicals have aromatic and quinoidal characteristics, respectively. Inspection of their calculated electronic structures shows that, in comparison to $^3\mathbf{2}^{\cdot\cdot}$, one of the spins in $^3\mathbf{2}^{\cdot\cdot}*$ is more delocalized onto arene-rings linked to the TMM framework.

The trimethylenemethane[1] (TMM, Fig. 1) biradical is a representative non-Kekulé molecule that has a triplet ground state (T_0) owing to its D_{3h} symmetry and pair of degenerate singly-occupied molecular orbitals (SOMOs). As a result of this characteristic, many theoretical and experimental studies have been carried out probing the curious electronic structures and magnetic properties of TMM biradicals.[2] The fact that these biradicals emit triplet–triplet ($T_1 \rightarrow T_0$) fluorescence has received great attention.[3,4]

In previous studies, Matsui, Ikeda, and coworkers described the observation of $T_1 \rightarrow T_0$ fluorescence from the excited states of the 1-methyl-1-phenyl-, 1,1-diphenyl-, and 1-(2-naphthyl)-1-phenyl-substituted TMM biradicals, $^3\mathbf{2a}$–$\mathbf{c}^{\cdot\cdot}*$ (Scheme 1). For this purpose, thermoluminescence (TL)[5] and two-color two-laser flash photolysis measurements were conducted using the corresponding aryl-substituted methylenecyclopropanes **1a–c**.[6] Moreover, $T_1 \rightarrow T_0$ fluorescence of these biradicals was utilized as the basis for the design of a new organic light-emitting diode, termed "organic radical light-emitting diode".[5a]

The electronic configurations of the excited T_1 states of the TMM biradicals are complicated by their multi-configuration character. Additionally, electronic transition wavelengths and T_0 geometries of compound $^3\mathbf{2b}$, computed using time-dependent (TD) density functional theory (DFT)[6] with the B3LYP/cc-pVDZ method, are considerably different from the absorption and emission wavelengths observed experimentally.[7] Thus, more accurate and rigorous *ab initio* quantum chemical studies, and a detailed analysis of geometry relaxation occurring in the T_1 state are required to have a greater understanding of the electronic structures of the excited states of TMM biradicals.

In the investigation described below, we carried out a theoretical study of the triplet–triplet fluorescence mechanism to accurately predict structural, electronic and $T_1 \rightarrow T_0$ emission properties of triplet aryl-substituted trimethylenemethane biradicals $^3\mathbf{2}^{\cdot\cdot}*$. *Ab initio* post-Hartree–Fock methods and three

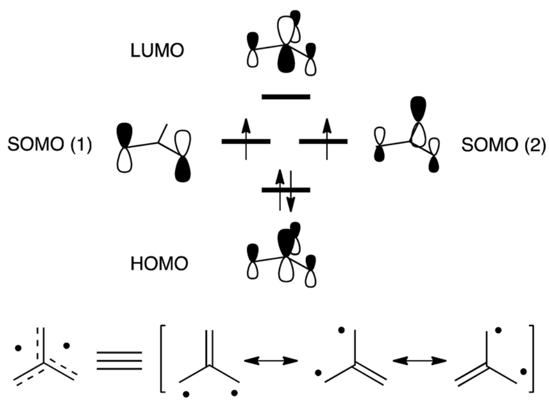

Fig. 1 (Top) Frontier molecular orbitals of the parent TMM biradical and (bottom) its corresponding Lewis resonance structures.

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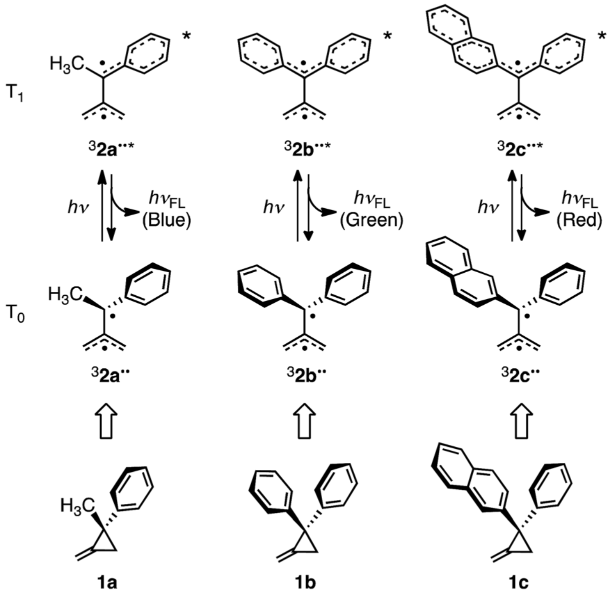


Scheme 1 Chemical structures of **1a–c** and electronic structures of $^{3}\mathbf{2a–c}^{\bullet\bullet}$ and $^{3}\mathbf{2a–c}^{\bullet\bullet}*$ associated with T$_0$–T$_1$ and T$_1$–T$_0$ transitions accompanying fluorescence.

different (TD-)DFT functionals were used for this purpose. When treating open-shell systems, DFT methods often suffer from spin contamination, which usually is more severe when excited rather than ground states are computed. To validate the (TD-)DFT results, high-level *ab initio* benchmark calculations where carried out on $^{3}\mathbf{2}^{\bullet\bullet}$ and the calculated spin densities and excitation energies obtained by using both types of methods were compared. In this effort, the triplet excited states of three model aryl-substituted TMM biradicals were theoretically studied because they each emit one of the three primary colors (blue, green, and red) (Scheme 1).[5a]

All (TD-)DFT geometry optimizations were performed using the spin-unrestricted UB3LYP, UM06-2X, and CAM-UB3LYP functionals[8] in conjunction with the 6-31G(d) basis set.[9] (TD-)DFT single point energies were obtained using the same methods, however, the larger 6-311+G(d)[9c] basis set was employed. For the smallest, methyl-phenyl substituted biradical, $^{3}\mathbf{2a}^{\bullet\bullet}$, complete *ab initio* active space self-consistent field (CASSCF)[10] single point energy calculations with 10 π-orbitals and 10 electrons were performed, followed by a multireference second-order Møller–Plesset perturbation (MRMP2) treatment.[11] All DFT calculations were conducted using Gaussian 09,[12] while the GAMESS-US[13] and MOLPRO[14] program packages were employed for the post-Hartree–Fock calculations. Below, we will refer to T$_1$ and T$_0$ states of $\mathbf{2}^{\bullet\bullet}$ simply as $^{3}\mathbf{2}^{\bullet\bullet}*$ and $^{3}\mathbf{2}^{\bullet\bullet}$, respectively.

In the first phase of this study, molecular geometry optimizations were carried out on $^{3}\mathbf{2a–c}^{\bullet\bullet}$ and $^{3}\mathbf{2a–c}^{\bullet\bullet}*$ using various DFT functionals.[15] The geometries of triplet ground (T$_0$) and excited (T$_1$) states of these biradicals, obtained by using UB3LYP/6-31G(d), are displayed in Fig. 2, and selected bond lengths are listed in Table 1. The lengths of the C5–C6, C6–C7 and C7–C8 bonds (see Fig. 2 for atom numbering) for $^{3}\mathbf{2a}^{\bullet\bullet}$ are in the range of 1.39–1.42 Å, which is typical for benzene-rings having a small degree of bond alternation. The results of applying a simulated harmonic oscillator model of the aromaticity (HOMA)[16] of the phenyl group in $^{3}\mathbf{2a}^{\bullet\bullet}$ (0.927) suggests that its aromaticity is relatively high (*i.e.*, roughly equal to that of benzene). In contrast, the respective C5–C6, C6–C7 and C7–C8 bond lengths in $^{3}\mathbf{2a}^{\bullet\bullet}*$ are 1.47, 1.37, and 1.44 Å, suggesting that the degree of bond alternation is higher than in the ground state and, as a result, that the aromatic character of the phenyl group is reduced upon excitation to the T$_1$ state. The greatly lower HOMA value (0.187) calculated for the phenyl group of $^{3}\mathbf{2a}^{\bullet\bullet}*$ also indicates that its aromaticity is strongly reduced.

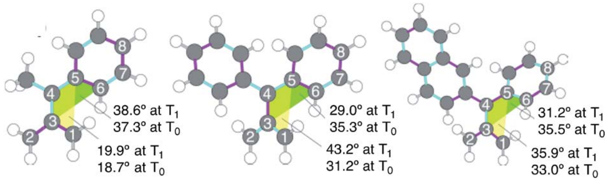


Fig. 2 Optimized structures and atom labeling of (left) $^{3}\mathbf{2a}^{\bullet\bullet}*$, and (center) $^{3}\mathbf{2b}^{\bullet\bullet}*$, and (right) $^{3}\mathbf{2c}^{\bullet\bullet}*$. Pink and blue bonds indicate elongated and shortened bonds of $^{3}\mathbf{2}^{\bullet\bullet}*$ relative to $^{3}\mathbf{2}^{\bullet\bullet}$.

The changes in the C–C bond lengths taking place in proceeding from the diphenyl-substituted TMM biradical, $^{3}\mathbf{2b}^{\bullet\bullet}$, to $^{3}\mathbf{2b}^{\bullet\bullet}*$ are similar but somewhat less pronounced in comparison to those seen for the $^{3}\mathbf{2a}^{\bullet\bullet}$/$^{3}\mathbf{2a}^{\bullet\bullet}*$ system (Table 1). The calculated HOMA value changes are in accord with the reduction of aromaticity taking place in the phenyl group of $^{3}\mathbf{2a–b}^{\bullet\bullet}$ upon electronic excitation, with the largest change occurring in the monophenyl-substituted TMM biradical $^{3}\mathbf{2a}^{\bullet\bullet}$. On the other hand, the calculated bond lengths and HOMA values for $^{3}\mathbf{2c}^{\bullet\bullet}$/$^{3}\mathbf{2c}^{\bullet\bullet}*$ deviate from this trend. In this case, the degree of aromaticity of the single phenyl group is less affected by excitation, presumably because excitation is localized mainly in the larger π-conjugated naphthyl group. The calculated dihedral angles composed of C1–C3–C4–C5 (yellow, Fig. 2) and C3–C4–C5–C6 (green) for the $^{3}\mathbf{2}^{\bullet\bullet}$/$^{3}\mathbf{2}^{\bullet\bullet}*$ systems also follow these trends.

An analysis of their electronic structures provides further information about the nature of the excited TMM biradicals $^{3}\mathbf{2}^{\bullet\bullet}*$. Spin distributions of $^{3}\mathbf{2a–c}^{\bullet\bullet}$ and $^{3}\mathbf{2a–c}^{\bullet\bullet}*$ at Franck–

Table 1 Geometry parameters of $^{3}\mathbf{2a–c}^{\bullet\bullet}$ and $^{3}\mathbf{2a–c}^{\bullet\bullet}*$ Obtained by using (TD-)UB3LYP/6-31G(d)

	Bond lengths/Å					
Biradicals	C3–C4	C4–C5	C5–C6	C6–C7	C7–C8	HOMA[a]
$^{3}\mathbf{2a}^{\bullet\bullet}$	1.45	1.46	1.42	1.39	1.40	0.927
$^{3}\mathbf{2a}^{\bullet\bullet}*$	1.44	1.44	1.47	1.37	1.44	0.187
$^{3}\mathbf{2b}^{\bullet\bullet}$	1.47	1.47	1.42	1.39	1.40	0.929
$^{3}\mathbf{2b}^{\bullet\bullet}*$	1.49	1.43	1.45	1.37	1.42	0.583
$^{3}\mathbf{2c}^{\bullet\bullet}$	1.47	1.47	1.42	1.39	1.40	0.931
$^{3}\mathbf{2c}^{\bullet\bullet}*$	1.47	1.45	1.39	1.42	1.40	0.896

[a] Aromaticity indices of the phenyl group.

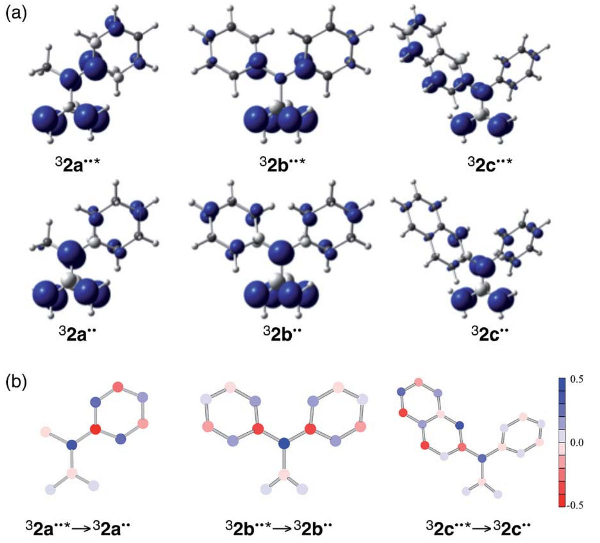


Fig. 3 (a) Spin distributions for $^{3}\mathbf{2a{-}c}^{\bullet\bullet}$ and $^{3}\mathbf{2a{-}c}^{\bullet\bullet *}$ at Franck–Condon geometries. Blue and gray represent positive and negative areas of spin densities, respectively. (b) T_1–T_0 difference charges occurring in the $^{3}\mathbf{2}^{\bullet\bullet *} \rightarrow {}^{3}\mathbf{2}^{\bullet\bullet}$ transitions calculated from natural orbitals for α- and β-spin. Red and blue represent the increase and decrease of α-spin density, respectively, upon excitation.

Condon geometries were determined at the (TD-)UB3LYP/6-31G* level of theory (Fig. 3a). The results show that the spin densities of both $^{3}\mathbf{2a}^{\bullet\bullet}$ and $^{3}\mathbf{2b}^{\bullet\bullet}$ are almost completely localized at C4 (benzylic), C1 (allylic), and C2 (allylic). For $^{3}\mathbf{2a{-}c}^{\bullet\bullet}$, the spin densities at C1 and C2 are almost identical to those of the corresponding ground state, $^{3}\mathbf{2a{-}c}^{\bullet\bullet}$. In contrast, the spin density at C4 of $^{3}\mathbf{2a}^{\bullet\bullet *}$ is located close to the ipso-position (C5) of the phenyl group. The change taking place in spin densities at each atom in the $^{3}\mathbf{2b}^{\bullet\bullet} \rightarrow {}^{3}\mathbf{2b}^{\bullet\bullet *}$ transition is similar to those occurring in the $^{3}\mathbf{2a}^{\bullet\bullet} \rightarrow {}^{3}\mathbf{2a}^{\bullet\bullet *}$ transition. Interestingly, the spin density changes caused by the $^{3}\mathbf{2c}^{\bullet\bullet} \rightarrow {}^{3}\mathbf{2c}^{\bullet\bullet *}$ transition occur most prominently in the 2-naphthyl group. The alterations in electronic structure are consistent with the geometrical changes that take place in all of the $^{3}\mathbf{2}^{\bullet\bullet} \rightarrow {}^{3}\mathbf{2}^{\bullet\bullet *}$ transitions (see the discussion in the previous section).

To express the spin distribution changes that take place in $^{3}\mathbf{2}^{\bullet\bullet *} \rightarrow {}^{3}\mathbf{2}^{\bullet\bullet}$ transitions in a quantitative manner, we express the difference in the spin density of the ith atom, $N_i^{T_1-T_0}$ by the equation given in eqn (1),

$$N_i^{T_1-T_0} = \left(\alpha_i^{T_1} - \beta_i^{T_1}\right) - \left(\alpha_i^{T_0} - \beta_i^{T_0}\right) \tag{1}$$

where $\alpha_i^{T_1/T_0}$ and $\beta_i^{T_1/T_0}$ are the respective natural spin densities estimated from α and β natural orbitals for $^{3}\mathbf{2}^{\bullet\bullet *}$ and $^{3}\mathbf{2}^{\bullet\bullet}$ (see Tables S7–S9†). Inspection of the data listed in Fig. 3a shows that the spin distributions at C1, C2 and C3 (the allyl moiety) do not significantly change during the $^{3}\mathbf{2}^{\bullet\bullet *} \rightarrow {}^{3}\mathbf{2}^{\bullet\bullet}$ transition. Moreover, the sum of their spin densities is approximately 1.1 each for $^{3}\mathbf{2a{-}c}^{\bullet\bullet}$ and $^{3}\mathbf{2a{-}c}^{\bullet\bullet *}$ (see Table S10†). Thus, it appears that one unpaired electron is delocalized over the allyl moieties of both $^{3}\mathbf{2a{-}c}^{\bullet\bullet}$ and $^{3}\mathbf{2a{-}c}^{\bullet\bullet *}$. The other unpaired electron in the T_1 excited state ($^{3}\mathbf{2}^{\bullet\bullet *}$) is delocalized over the remainder of the molecule, whereas it is localized on C4 in $^{3}\mathbf{2a{-}c}^{\bullet\bullet}$. The electronic structure change occurring upon excitation is also made apparent by inspection of the flow of spin density from C4 to C5 (Fig. 3b). The excitation-promoted, spin density reorganization decreases on proceeding from $^{3}\mathbf{2a}^{\bullet\bullet}$ to $^{3}\mathbf{2c}^{\bullet\bullet}$. In addition, introduction of benzene or naphthalene rings leads to an enhancement in electron delocalization in the T_0 state (Tables S7–S9†). The analysis presented above indicates that electronic structures of $^{3}\mathbf{2a{-}c}^{\bullet\bullet}$ and $^{3}\mathbf{2a{-}c}^{\bullet\bullet *}$ can be schematically depicted in the manner shown in Scheme 1. As a result, the distribution of the second unpaired electron is controlled by introduction of aromatic groups on the TMM biradical backbone (*e.g.*, $^{3}\mathbf{2c}^{\bullet\bullet}$).

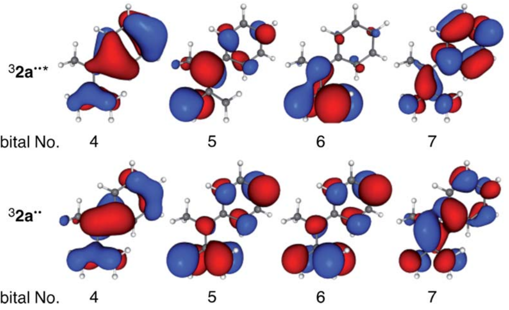
Previously, Ikeda and co-workers experimentally determined the wavelength maxima for $T_1 \rightarrow T_0$ fluorescence of $^{3}\mathbf{2}^{\bullet\bullet *}$ by using TL methods.[5a] The TL maxima of $^{3}\mathbf{2a}^{\bullet\bullet *}$, $^{3}\mathbf{2b}^{\bullet\bullet *}$ and $^{3}\mathbf{2c}^{\bullet\bullet *}$ in methylcyclohexane matrices at *ca.* 130 K are 451, 501, and 602 nm, respectively. In the present work, we calculated the fluorescence wavelengths of $^{3}\mathbf{2a{-}c}^{\bullet\bullet *}$ using various TD-DFT functionals (Table 2). Interestingly, the fluorescence wavelengths obtained by using the UB3LYP method match well with the experimentally determined values.[5] Although use of the UM06-2X method also gives maxima that are close to the experimental values, it slightly overestimates the excitation energies. Utilization of the long-range corrected CAM-UB3LYP functional does not lead to improved results, suggesting that charge-transfer interactions are not important in $^{3}\mathbf{2}^{\bullet\bullet *}$. The use of UHF in this functional for treatment of large electronic separations suffers from a more serious spin contamination ($\langle S^2 \rangle$ ~2.54–4.01), especially in the case of $^{3}\mathbf{2c}^{\bullet\bullet}$.

Table 2 Fluorescence wavelength maxima (λ_{Em}) and oscillator strengths (f) of TMM biradicals obtained by experimental and various TD-DFT methods

	Exp[a]	TD-DFT[b]		
	TL	UB3LYP	UM06-2X	CAM-UB3LYP
Biradical	λ_{TL}/nm	λ_{Em}/nm ($\langle S^2\rangle, f$)	λ_{Em}/nm ($\langle S^2\rangle, f$)	λ_{Em}/nm ($\langle S^2\rangle, f$)
$^{3}\mathbf{2a}^{\bullet\bullet}$	451	443 (2.43, 0.003)	438 (2.28, 0.005)	440 (3.10, 0.001)
$^{3}\mathbf{2b}^{\bullet\bullet}$	501	479 (2.24, 0.010)	464 (2.23, 0.018)	443 (2.54, 0.007)
$^{3}\mathbf{2c}^{\bullet\bullet}$	602	613 (2.63, 0.002)	554 (2.39, 0.004)	903 (4.01, 0.000)

[a] From ref. 5*a*. [b] The 6-311+G(d) and 6-31G(d) basis sets were employed for single point calculations and optimizations, respectively.

Table 3 NOON Values of **32a**$^{\cdot\cdot}$ and ^{3}**2a**$^{\cdot\cdot}$* obtained using CASSCF(10o, 10e) calculations



NOON	Orbital no.	1	2	3	4	5	6	7	8	9	10
	^{3}**2a**$^{\cdot\cdot}$*	1.92	1.90	1.88	1.47	1.02	0.97	0.55	0.12	0.09	0.07
	2a$^{\cdot\cdot}$	1.96	1.92	1.90	1.87	1.00	1.00	0.13	0.10	0.08	0.04

To validate the (TD-)DFT results presented above, the electronic configuration of ^{3}**2a**$^{\cdot\cdot}$* was evaluated by employing post-Hartree–Fock CASSCF and multireference MP2 calculations. First, 10 π-orbitals of ^{3}**2a**$^{\cdot\cdot}$ were obtained using the RHF/6-311+G(d) method for the singlet spin state. Subsequent CASSCF calculations were carried out using a full π-orbital (10e, 10o) active space for the triplet ground state. In Table 3 are listed the corresponding natural orbital occupation numbers (NOON), where 2, 1, and 0 indicates doubly-, singly-, and un-occupied orbitals, respectively. Importantly, a deviation of NOON from integer numbers implies that the wavefunction has multireference character.[17] Analysis of the NOON values for ^{3}**2a**$^{\cdot\cdot}$ indicates the existence of four doubly-occupied (NOON > 1.87), two singly-occupied (NOON ~ 1.00), and four un-occupied (NOON < 0.13) orbitals within the active space. On the other hand, the NOON values of orbitals numbers 4 and 7 in ^{3}**2a**$^{\cdot\cdot}$* deviate largely from integer values, signaling that the wavefunction has multireference character. Except for natural orbitals 4–7, the NOON values and orbital shapes of ^{3}**2a**$^{\cdot\cdot}$* and ^{3}**2a**$^{\cdot\cdot}$ are almost identical. The singly-occupied natural orbital of ^{3}**2a**$^{\cdot\cdot}$ is localized on the TMM moiety, while singly occupied natural orbitals of ^{3}**2a**$^{\cdot\cdot}$* (Table 3) are delocalized on the phenyl group. The fact that this finding is consistent with the natural charge distributions obtained by using (TD-)DFT calculations (Fig. 3) validates the DFT-based results.

The CASSCF-determined emission energy of the benchmark model ^{3}**2a**$^{\cdot\cdot}$ is 2.62 eV (473 nm) and that arising from MRMP2 is 2.51 eV (495 nm). The MRMP2 result is in good agreement with that determined experimentally (2.74 eV, 451 nm), and the TD-DFT determined emission energy (2.82 eV, 440 nm) is also close to the experimental value. These findings suggest that a well-balanced use of dynamic and non-dynamic correlations is necessary for quantitatively accurate assessment of the emission wavelengths of ^{3}**2**$^{\cdot\cdot}$*. The somewhat surprising similarity of the MRMP2 and UB3LYP results show that conceptually more simple density functional approaches can be applied to the complex electronic and molecular structures of ^{3}**2**$^{\cdot\cdot}$*. This is most likely a consequence of fortuitous error compensations.

In conclusion, studies aimed at understanding the T_1–T_0 fluorescence of aryl-substituted TMM biradicals ^{3}**2**$^{\cdot\cdot}$* were carried out using quantum chemical calculations. The results of calculations using high-level *ab initio* and various DFT functionals reveal that the wavefunctions of ^{3}**2**$^{\cdot\cdot}$* possesses significant multireference character. However, use of DFT approaches with sufficiently large basis sets leads to predictions of reasonable emission wavelengths of ^{3}**2**$^{\cdot\cdot}$*. In addition, the calculated changes of bond lengths and spin distributions demonstrate that significant relaxation of molecular geometries occurs in T_1 on going from an aromatic ground state to quinoid structured excited state. The overall results of this work demonstrate that it is possible to use DFT-based methods to estimate accurately the fluorescence properties of organic open-shell species.[18] This ability should accelerate the development and application of luminescent radical materials.

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