Elucidating the Electronic Structure of a Delayed Fluorescence Emitter via Orbital Interactions, Excitation Energy Components, Charge-Transfer Numbers, and Vibrational Reorganization Energies

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Abstract: Recently, Wang and co-workers carried out frontier molecule orbital engineering in the design of m-Cz-BNCz, a thermally activated delayed fluorescence (TADF) molecule that emits pure green light at an external quantum efficiency of 27%. To further understand the underlying molecular design principles, we employed four advanced electronic structure analysis tools. First, an absolutely localized molecular orbitals (ALMO-) based analysis indicates an antibonding combination between the highest occupied molecular orbitals (HOMOs) of the donor 3,6-di-tert-butylcarbazole fragment and the acceptor BNCz fragment, which raises the HOMO energy and red-shifts the fluorescence emission wavelength. Second, excitation energy component analysis reveals that the S1−T1 gap is dominated by two-electron components of the excitation energies. Third, charge transfer number analysis, which is extended to use fragment-based Hirshfeld weights, indicates that the S1 and T1 excited states of m-Cz-BNCz (within time-dependent density functional theory) have notable charge transfer characters (27% for S1 and 12% for T1). This provides a balance between a small single-triplet gap and a substantial fluorescence intensity. Last, a vibrational reorganization energy analysis pinpoints the torsional motion between the BNCz and Cz moieties of m-Cz-BNCz as the source for its wider emission peak than that of p-Cz-BNCz. These four types of analyses are expected to be very valuable in the study and design of other TADF and functional dye molecules.

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hermally activated delayed fluorescence (TADF) materials, which are known as the third generation of organic electroluminescent materials, can harvest all the currently generated singlet and triplet excitons for fluorescence and achieve 100% internal quantum efficiency (IQE).1−5 The key to the occurrence of the delayed fluorescence is an efficient reverse intersystem crossing (RISC) process within a TADF molecule, which requires a relatively small energy gap and a large spin−orbit coupling (SOC) between the S1 and T1 states.6−8 A minimized S1−T1 energy gap can be achieved through a pair of marginally overlapped frontier orbitals, and thus many earlier TADF molecules were developed with a twisted intramolecular charge-transfer (TICT) character.9−13 However, because of the dominating CT character of the transition of S1 back to S0, the emission spectra of such twisted TADF molecules are usually severely broadened (with a full-width at half-maximum (fwhm) around 70−100 nm), thus failing to provide the desired purity for high-resolution displays.14−17

A dedicated design strategy, known as multiresonance-induced TADF (MR-TADF), has been reported by Hatakeyama et al. in 2016.18 Within this strategy, electron-deficient atoms (such as boron) and electron-rich atoms (such as nitrogen) are oppositely placed in a rigid polycyclic aromatic framework, rendering the frontier orbitals effectively separated via multiple resonance effects. A series of MR-TADF molecules have been designed and synthesized, with extremely narrow bandwidth (fwhm around 20 nm) and excellent electroluminescent performance.19−23 Nevertheless, due to the structural similarity, most of the reported MR-TADF molecules are blue-light emitters.18−22 This has inspired the development of MR-TADF molecules with other emission wavelengths.

An exciting breakthrough of MR-TADF materials with green emission was reported recently by Wang and co-workers via frontier molecular orbital engineering (FMOE).24 The target molecule, m-Cz-BNCz (shown in Figure 1), which combines a B−N containing MR frame (BNCz) with a 3,6-di-tert-butylcarbazole substituent (DtBuCz, shortened as “Cz” in this Letter), was successfully employed as an emitter to fabricate pure green organic light-emitting diodes (OLEDs) with a maximum external quantum efficiency (EQE) of 27%. In contrast, the p-Cz-BNCz isomer emits blue light.

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To fully understand the remarkable performance of the m-Cz-BNCz emitter, additional theoretical insights of its electronic structural and photophysical properties are needed, especially in the case of the red-shifted spectra compared to its para-substituent isomer, p-Cz-BNCz. This will be achieved in this Letter by employing the four latest electronic structure analysis tools.

**ALMO-Based Orbital Interactions Analysis.** To decipher the difference in the electronic structural and photophysical properties of m-Cz-BNCz and p-Cz-BNCz, we divide these complexes into two fragments, BNCz and Cz, which are linked together by a C−N bond. A quantitative analysis of interactions between orbitals on covalently linked fragments in a molecular complex was developed by Mao and co-workers, which allows us to go beyond a qualitative interpretation of the frontier orbitals of these complexes and quantify their key fragment contributions. This analysis is built upon the ALMO analysis from the Head-Gordon group and closely resembles the in situ block-localized wave function analysis from Mo and co-workers. Here we shall briefly outline our analysis procedure implemented within a development version of Q-CHEM 5.2. To properly describe excited states with a partial charge-transfer character, we employ LRC-ωPBE, a range-separated hybrid functional, with an optimally tuned ω value obtained for each molecule following the procedure in ref 38. This functional was reported to best describe the electronic structure of TADF molecules within the TDDFT framework of theory.

- **Step I.** Build the “isolated” state by constructing isolated fragments and obtaining their respective fragment orbitals. For covalently linked fragments, such as those in m-Cz-BNCz and p-Cz-BNCz, the main fragment (BNCz) can be terminated with a hydrogen link atom, while the attached fragment (Cz) can be saturated with a benzene ring. Standard self-consistent field (SCF) calculations are performed for each saturated fragment. Orbital localization is then carried out to identify (i) the C−H bond orbital in BNCz−H associated with the hydrogen link atom and (ii) the bridge C−N bond orbital and benzene orbitals of Cz−Ph. SCF calculations are then performed again with the identified bond orbitals frozen to obtain the other orbitals that are truncated and “absolutely localized” on fragments, 𝜓_{FRAG}.

- **Step II.** Construct the “frozen” state. Fragment orbitals are combined together without relaxation (𝜓_{FRZ} = 𝜓_{FRAG}) and then antisymmetrized to obtain a “frozen” state. Its difference from the “isolated” state corresponds to the effects of permanent electrostatics and exchange-repulsion on the frontier orbitals.

- **Step III.** Construct the “polarized” state (also called the ALMO state). Two sets of fragment orbitals are allowed to polarize each other while restricted to stay localized on each fragment. This leads to the “polarized” state of the system with fully polarized fragment orbitals, 𝜓_{POL}.

- **Step IV.** Analyze the interaction between polarized fragment orbitals. This is done by projecting the conventional MOs, 𝜓_{FULL}, onto the polarized fragment orbitals.
\[ \psi_q^{\text{FULL}} = \sum_{x_p} \psi_{q,x_p}^{\text{POL}} \]  

(1)

\[ \psi_{q,x_p}^{\text{POL}} = \left( \psi_{q,x_p}^{\text{POL}} \right) \]

(2)

Note that in eq 2, contravariant fragment orbitals, \( \psi_{q,x_p}^{\text{POL}} \), are used to ensure proper projections within the space spanned by two sets of fragment MOs, which are nonorthogonal to each other with an overlap \( S_{x_p,x_p'} \).

\( m\text{-Cz-BNCz} \). As illustrated in Figure 2, the HOMO of the complex, \( m\text{-Cz-BNCz} \), is composed by HOMOs from both the donor (Cz) and acceptor (BNCz), with mixing coefficients 0.76 and −0.63, respectively. Across the C–N bond between the two fragments, the phase of the \( m\text{-Cz-BNCz} \) HOMO changes from red (on BNCz carbon) to blue (on Cz nitrogen), which indicates an antibonding (destructive) combination. Such an antibonding combination raises the (nearly degenerate) fragment HOMO energies of \( 6.517 \text{ eV} \) (BNCz) and \( 6.517 \text{ eV} \) (Cz) to the value of \( −6.216 \text{ eV} \) for the \( m\text{-Cz-BNCz} \) complex.

In contrast, the LUMO of the BNCz fragment contributes exclusively to the LUMO of the complex, with its orbital energy increased slightly from \( −1.133 \) to \( −1.066 \text{ eV} \). This is also confirmed by the fragment and complex LUMOs in the figure, which look essentially identical. In general, a substantial overlap between orbitals from different fragments is needed for them to interact strongly and mix together. Clearly, the BNCz LUMO has a nearly zero overlap with Cz HOMO because of their different symmetries around the C–N bond. BNCz LUMO also has a very small overlap with Cz LUMO (shown on the top right of Figure 2), as they are spatially separated.

Putting these together, less energy is needed to excite an electron from an elevated HOMO into a largely unchanged LUMO, causing a red-shift in the HOMO → LUMO excitation compared to BNCz.

\( p\text{-Cz-BNCz} \). For the para-substituted isomer, as depicted in Figure 3, both its HOMO and LUMO come directly from the BNCz fragment, while the Cz fragment has little role in the composition of the complex’s two frontier orbitals. This suggests that both the HOMO and LUMO remained localized on the BNCz fragment, with the corresponding energies raised marginally by 0.096 and 0.228 eV, respectively. Specifically, the BNCz HOMO (shown on the bottom left of Figure 3) and Cz HOMO (similar to the one on the bottom right of Figure 2) have different symmetry around the C–N bond of the para-substituted isomer. A nearly zero overlap between the HOMOs prevents a strong interaction between and a mixing of these two orbitals. On the other hand, the slightly larger increase in the LUMO energy arises from a very small antibonding contribution from the nitrogen atom of the Cz fragment, which agrees with the experimentally observed small blue shift in the emission energy.

When it comes to FMOE, the Cz substitution group behaves like an electron donating group (EDG), whose HOMO has a considerable weight on the nitrogen atom. To exert a noticeable effect on the fluorophore electronic properties, the HOMO of an EDG needs to be mixed into the fluorophore HOMO (with a similar energy) and with a linkage that allows a substantial overlap between the fluorophore and substituent HOMOs. As the BNCz fluorophore HOMO has a much larger weight on the meta site than on the para site, only a linkage at the meta-site leads to a “head-on” overlap between the two orbitals and, consequently, a substantial increase of the HOMO energy.

**Excitation Energy Component Analysis.** The ALMO-based frontier orbital analysis above provides a theoretical basis for the narrowing of HOMO–LUMO gap in \( m\text{-Cz-BNCz} \) compared to BNCz as well as a slightly wider HOMO–LUMO gap in \( p\text{-Cz-BNCz} \). However, to gain a quantitative understanding of shifts in fluorescence energies and singlet–triplet splittings, it is expedient to venture beyond the HOMO–LUMO picture and consider other components of the excitation energy. To do so, we decompose the excitation energies into a sum of four 1-electron terms and three 2-electron terms, as described in refs 42 and 43. For the first six vertical excitation energies for each molecule (at corresponding \( S_0 \) geometries), the results are shown in Figure 4 while the full underlying numerical data of all seven terms are provided in Table S10.

Within the TDDFT-TDA theory, the \( S_1 \) excitation energies are 2.719 eV (\( m\text{-Cz-BNCz} \) < 2.975 eV (BNCz) < 2.996 eV (\( p\text{-Cz-BNCz} \)), which follows exactly the same trend as the observed emission wavelengths. The 2-electron contributions to the \( S_1 \) excitation energies (shown as the red bars in Figure 4 due to their negative values) are clearly very similar across these systems, with numerical values of −2.640, −2.893, and −2.741 eV, respectively. In contrast, the 1-electron contributions (shown as the blue bars in Figure 4) are 5.358 eV (\( m\text{-Cz-BNCz} \)), 5.868 eV (BNCz), and 5.737 eV (\( p\text{-Cz-BNCz} \)), which are primarily responsible for the difference between the computed excitation energies. This reaffirms the validity of our ALMO-based frontier orbital-interactions analysis in interpreting spectral shifts.

TDDFT-TDA calculations predict the vertical \( S_1 \rightarrow T_1 \) energy gaps \( ^{35} \) to be 0.404 eV (\( m\text{-Cz-BNCz} \) < 0.475 eV (\( p\text{-Cz-BNCz} \) < 0.483 eV (BNCz), which should facilitate RISC for \( m\text{-Cz-BNCz} \). Explaining the \( S_1 \rightarrow T_1 \) gaps based on the HOMO–LUMO transition and an analysis of the 2-electron terms is unavoidable. Indeed, Figure 4 demonstrates that the \( S_1 \rightarrow T_1 \) energy gaps are primarily caused

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**Figure 3.** ALMO analysis of the interactions between BNCz and Cz frontier orbitals to produce the fully converged MOs of \( p\text{-Cz-BNCz} \) complex using the LRC-ωPBE functional with an optimally tuned \( \omega \) value of 0.140 \( \alpha_0^{-1} \) and the 6-311G(d,p) basis set. All orbital energies are in eV. An isovalue of 0.02 au is used for the MO plots. Numerical values in black refer to projection coefficients, which are calculated based on eq 2.
by the 2-electron components. Traditionally, the splitting between $S_1$ and $T_1$ is explained via the exchange integral between HOMO and LUMO\(^{11}\) and this term can be generalized as the self-repulsion of the transition density evaluated as a 2-electron component of the excitation energy.\(^{42}\) This term destabilizes singlets but has no effect on triplets and, thus, increases the gap between them. (Note that, with global or range-separated hybrid functionals, a similar term with a scaled $\omega$-PBE functional (with $\omega$ values of 0.154 $a_0^{-1}$, 0.136 $a_0^{-1}$ and 0.140 $a_0^{-1}$, respectively) and the 6-311G(d,p) basis set.

![Excitation Energy Components](image)

**Figure 4.** Excitation energy decomposition of the lowest six TDDFT-TDA excited states of BNCz, m-Cz-BNCz, and p-Cz-BNCz calculated using the LRC-$\omega$PBE functional (with $\omega$ values of 0.154 $a_0^{-1}$, 0.136 $a_0^{-1}$ and 0.140 $a_0^{-1}$, respectively) and the 6-311G(d,p) basis set.

The remaining energy is distributed among the 1-electron term, which represent the percentage contribution from the charge-transfer excitation ($F \neq F'$) and local excitation ($F = F'$).

Different fragment partitioning schemes, such as Mulliken, Löwdin, and fragment-based Hirshfeld (FBH), are employed to compute the fragment $S_{ab,F}$ and $S_{ij,F}$ matrices, whose calculations are detailed in Section S1.1 of the Supporting Information.

**m-Cz-BNCz.** For the meta-substituted isomer, the charge-transfer numbers are computed for the lowest three singlet and triplet excited states using eq 7. Their values are tabulated in Table S1 and FBH values are illustrated in Figure 5a. The $S_1$ state, which is dominated by the HOMO $\rightarrow$ LUMO excitation (amplitude: 0.9611) and has a vertical excitation energy of 2.7182 eV, is shown to be a mixed local excitation (LE)/charge transfer (CT) state, with 71.61% (within the FBH population scheme) from local excitation within BNCz; 21.72% from a charge transfer from Cz to BNCz; and minor contributions from...
reverse charge transfer (0.74%) and local excitation within Cz (0.43%). The T₁ state involves both HOMO → LUMO (amplitude: 0.9070) and HOMO−1 → LUMO (amplitude: 0.3347) transitions. Since HOMO−1 is localized on the BNCz fragment, the T₁ state has a larger LE contribution (86.64% within the FBH population scheme) and a smaller CT contribution (12.39%).

In Figure 5a, the charge transfer numbers for higher excited state indicate that both T₂ and T₃ are dominated by LE (94.86% and 88.77%, respectively), while S₂ and S₃ are mixed LE/CT states (with 38.73% and 70.69% of LE, respectively). The differences in state characters can be understood in terms of the interplay between the “K²” and “J²” terms discussed above. Singlets experience short-range exchange repulsion via “J²” and long-range Coulomb attraction via “K²” whereas triplets only experience the attractive “K²” term. As a consequence, one finds that low-energy triplet states are generally more confined and have reduced CT character and enhanced binding energies when compared to the related singlet states (see Section S2.2 for more details).

In general, the different LE/CT ratios in S₁ and T₁−T₃ are important for efficient RISC processes, as they facilitate larger SOC (see Table S17) and vibronic coupling. Note that, with T₂ and T₃ close in energy with the S₁ state, they might also play a role in the TADF process of m-Cz-BNCz. Within the thermal vibrational correlation function (TVCF) formalism, the T₂−T₁ transition rate is estimated to be ultrafast at 10¹³ s⁻¹ (see Table S18), suggesting that the RISC should be mainly from T₁. Further spin-vibronic studies on the roles of the

Figure 5. Charge-transfer numbers of the lowest six TDDFT-TDA excited states of m-Cz-BNCz and p-Cz-BNCz calculated using the LRC-ωPBE functional (with ω values of 0.136 a₀⁻¹ and 0.140 a₀⁻¹, respectively) and the 6-311G(d,p) basis set. The FBH fragment partitioning scheme is used.

Figure 6. Electronic vibrational coupling analysis and calculated absorption and photoluminescence spectra for m-Cz-BNCz and p-Cz-BNCz. Parts a and b depict the reorganization energy between Sₐ and Sₜ at Sₜ-optimized geometries for m-Cz-BNCz and p-Cz-BNCz, respectively, while parts c and d depict the corresponding projected reorganization energy onto internal coordinates (shown with the largest five components). Parts e and f are the absorption (Abs) and photoluminescence (PL) spectra of m-Cz-BNCz and p-Cz-BNCz computed via the TVCF formalism. Electronic vibrational coupling analysis as well as the calculation of spectra are performed with the B3LYP functional and 6-31G(d) basis set due to the limited availability of the analytical nuclear gradient and Hessian of the optimally tuned LRC-ωPBE functional.
T1 and T3 states will be pursued following strategies in refs 55 and 56.

A detailed comparison of the different population analysis schemes is shown in Table S1. At first sight, it appears surprising that the different population analysis schemes yield almost identical results in Table S1, even though a triple-$\zeta$ 6-311G(d,p) basis is used and Mulliken populations are known to be rather sensitive to the basis set size. However, it should be kept in mind that the charge-transfer numbers are computed as a sum over a whole molecular fragment and that the population analysis scheme should only affect the atoms immediately adjacent to the bond between the fragments.

p-Cz-BNCz. For this isomer, the charge-transfer numbers of its lowest excited states, as collected in Table S2, reveal a very different picture for the lowest singlet and triplet states. Now, both the S1 and T1 states are dominated by LE and Mulliken populations are known to be rather sensitive to the basis set size. This is expected because both the HOMO and LUMO of p-Cz-BNCz are shown to be localized on the BNCz moiety (Figure 3).

Among the higher-energy excited states of p-Cz-BNCz, S2 has a mixed LE and CT character, in which the weights of CT are larger than 66%. In contrast, T2, T3, and S3 are dominated by LE (larger than 56%). In contrast, T2, T3, and S3 are dominated by LE (larger than 56%).

Vibrational Reorganization Energy Analysis. The broadening of the absorption/photoluminescence spectra is closely related to the reorganization energy between the light-emitting state and the ground state of a given system. As proposed by Reimers in 2001, within the harmonic oscillator approximation, the total reorganization energy of a system can be evaluated via normal-mode analysis as

$$\lambda = \sum_i \lambda_i = \sum_i \frac{1}{2} \omega_i^2 \Delta Q_i^2$$

where $\lambda_i$ corresponds to the reorganization energy due to normal mode $i$ with frequency $\omega_i$, and $\Delta Q_i$ represents the displacement along the $i$th normal mode coordinate between the equilibrium position of the light-emitting state and the ground state. $\Delta Q_i$ can be further expressed as a linear combination of the internal coordinates,

$$\Delta Q_i = \sum_j \alpha_{ij} \Delta S_j$$

where $\Delta S_j$ corresponds to the displacement along the $j$th internal coordinate between the equilibrium position of the light-emitting state and the ground state. Substituting eq 9 into eq 8, one obtains the reorganization energy with respect to each internal coordinate,

$$\lambda = \sum_j \lambda_j + \sum_{j<k} \lambda_{jk} = \sum_{j<k} \frac{\omega_j^2 \omega_k^2}{2} \Delta S_j^2 + \sum_{j<k} \alpha_{jk} \alpha_{kj} \Delta S_j \Delta S_k$$

Here, $\lambda_j \equiv \sum (\alpha_j^2/2) \Delta S_j^2$ corresponds to the diagonal elements and $\lambda_{jk} \equiv \sum (\alpha_j \alpha_k/2) \alpha_j \alpha_k \Delta S_j \Delta S_k$ corresponds to the off-diagonal elements.

To further validate the role played by the Cz group in m-Cz-BNCz, we carry out the reorganization energy analysis between the S0 and S1 states (each optimized at the B3LYP/6-31G(d) level of theory) for both m-Cz-BNCz and p-Cz-BNCz using the molecular material property prediction package MOMAP 2020A.58–61 As shown in parts a and b of Figure 6, the reorganization energy of m-Cz-BNCz is significantly larger compared to that of p-Cz-BNCz, corresponding to a larger $S_1 \rightarrow S_0$ structural change of m-Cz-BNCz compared to its para-substituted counterpart. The extra flexibility of m-Cz-BNCz structure during its fluorescence lifetime mainly arises from the torsion between the center BNCz moiety and the carbazole group as indicated in parts c and d of Figure 6. For m-Cz-BNCz, the projected reorganization energies onto the dihedral angle between BNCz and Cz moieties are significant, while the corresponding parts in p-Cz-BNCz are negligible. The projected reorganization energies of these two molecules also underline the fact that the S1 state of m-Cz-BNCz has a marked charge-transfer character while the S1 state of p-Cz-BNCz is LE-dominated, which is consistent with the results of charge-transfer number analysis shown in Figure 5.

The theoretical absorption and photoluminescence spectra can be evaluated via the TVCF method as

$$\sigma_{\text{abs}} = \frac{4\pi}{3c} \sum_{\nu \nu} P_{\nu \nu}(T) \left( \Theta_{\nu \nu} \right)^{1/2}$$

where $P_{\nu \nu}(T)$ is the Boltzmann distribution function for the initial vibronic manifold; $\Theta_{\nu \nu}$ and $\Theta_{\nu \nu}$ are vibrational wave functions; $E_{\nu \nu}$ is the adiabatic energy gap between initial (final) and final (initial) electronic states; $E_{\nu \nu}$ and $E_{\nu \nu}$ are vibraional energies in the corresponding electronic states.

The absorption and photoluminescence spectra of m-Cz-BNCz and p-Cz-BNCz predicted via the TVCF formalism using MOMAP2020A are given in parts e and f of Figure 6. Due to the larger reorganization energy from the torsion between the BNCz and Cz moieties in m-Cz-BNCz, broader spectra are obtained compared to those of p-Cz-BNCz. The engagement of CT in the S1 state of m-Cz-BNCz also shifts the emission spectrum bathochromically to green light region, which distinguishes m-Cz-BNCz from other blue-light DABNA derivatives. Note that even though the emission spectrum of m-Cz-BNCz is broader compared to that of p-Cz-BNCz, its 43 nm fwhm according to the experimental result still makes it one of the purest green light-emitting complexes among various types of TADF materials.

Before concluding, we want to briefly discuss two methodological aspects: possible influences by the solvent environment and by the density functional. While the orbital interactions, excitation energy components, and charge transfer numbers are analyzed using the LRC-ωPBE functional for gas-phase molecules at their ground-state geometries, all results stay qualitatively the same upon the incorporation of solvent effects or with the adaption of different geometries and functionals. Indeed, a TDDFT/LR-PCM description of the toluene solvent leads to very similar charge transfer numbers in Tables S3 and S4 (compared to Tables S1 and S2) and excitation energy components in Table S11 (versus gas-phase results in Table...
S10). A more sophisticated TDDFT/ptSS-PCM treatment leads to rather small changes (< 0.1 eV) to the vertical excitation energies, as is evident in Table S14. Ground and excited-state energies in Table S19 for m-Cz-BNCz and p-Cz-BNCz at different geometries, together with the charge-transfer numbers of p-Cz-BNCz in Table S9 and its excitation energy components in Table S10 at its optimized S1 structure, indicate that our analysis results vary only slightly with the molecular geometry.

As far as the functional is concerned, the use of the B3LYP functional yields an expected more substantial charge-transfer character for the S1 and T1, states of m-Cz-BNCz, while retaining largely locally excited S1 and T1 states for p-Cz-BNCz (see Tables S5–S8). We caution that, although optimally tuned LRC-ωPBE well reproduced S1−T1 gaps for many other TADF molecules, the corresponding adiabatic S1−T1 gap is predicted to be 0.42 eV for m-Cz-BNCz (Table S19), which is much larger than the reported experimental value of 0.08 eV.24 This reaffirms the recently reported difficulty of TDDFT methods in accurately predicting singlet−triplet gaps for boron-rich MR-TADF molecules, a phenomenon that has been linked to intricate dielectric stabilization effects.50

To summarize, in this work, we have employed four powerful analysis tools to investigate a recently reported green-light TADF emitter, m-Cz-BNCz. The ALMO-based orbital interaction analysis reveals that the elevation of HOMO energy due to the antibonding mixing of the HOMOs of 3,6-di-tert-butyl-Cz and BNCz is responsible for the red shift in the emission wavelength (from blue to green), which contrasts with the case of p-Cz-BNCz, whose HOMO is almost entirely localized on the BNCz moiety. The consistency between trends in the frontier orbital gaps and emission wavelengths is further reassured by the results of our excitation energy component analysis, which also reveals that the two-electron components are crucial for the S1−T1 gaps. The charge-transfer number analysis shows that the S1 and T1 excited states of m-Cz-BNCz possess mixed LE/CT characters, wherein the contributions from the Cz → BNCz CT are 27% and 12%, respectively, while for p-Cz-BNCz both the S1 and T1 states are dominated by local excitation on the BNCz moiety. The mixed LE/CT nature of these states offers a desirable balance between a small S1−T1 gap and a substantial fluorescence intensity for m-Cz-BNCz, and the notable difference in the relative weights of CT can potentially lead to larger SOC between the S1 and T1 states and thereby facilitate efficient RISC. Finally, analysis of the vibrational reorganization energies for these two molecules reveals the extra flexibility of the structure of m-Cz-BNCz compared to its para-substituted counterpart arising from the torsion motion between the former’s BNCz and Cz moieties, which is related to the more significant CT character of m-Cz-BNCz’s S1 state and gives rise to its broader and bathochromically shifted emission peak than that of p-Cz-BNCz. These results have demonstrated that these analysis tools are well-suited for elucidating the structure−property relationship of TADF emitters, suggesting that they should be more widely used in computational modeling and rational design of functional molecules possessing attractive photophysical properties.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcllett.1c00094.

Details of the charge-transfer number calculation schemes and excitation energy decomposition methods; numerical results from BNCz, m-Cz-BNCz, and p-Cz-BNCz calculations, including charge-transfer numbers, excitation energy components, spin−orbit couplings, estimated transition rates, and solvation and geometry effects; and coordinates of optimized geometries (PDF)

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Notes

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