Theoretical Studies on the Photophysical Properties of the Ag(I) Complex for Thermally Activated Delayed Fluorescence Based on TD-DFT and Path Integral Dynamic Approaches

LingLing Lv,* Kun Yuan, TianYu Zhao, HuiXue Li, and YongCheng Wang

ABSTRACT: Theoretical calculation not only is a powerful tool to deeply explore photophysical processes of the emitters but also provides a theoretical basis for material renewal and design strategy in the future. In this work, the interconversion and decay rates of the thermally activated delayed fluorescence (TADF) process of the rigid Ag(dbp)(P2-nCB) complex are quantitatively calculated by employing the optimally tuned range-separated hybrid functional (ωB97X-D3) method combined with the path integral approach to dynamics considering the Herzberg–Teller and the Duschinsky rotation effects within a multimode harmonic oscillator model. The calculated results show that the small energy splitting ΔE(S1−T1) = 742 cm−1 (experimental value of 650 cm−1) of the lowest singlet S1 and triplet T1 state and proper vibrational spin–orbit coupling interactions facilitate the reverse intersystem crossing (RISC) processes from the T1 to S1 states. The kRISC rate is estimated to be 1.72 × 108 s−1 that is far more than the intersystem crossing rate kISC of 7.28 × 107 s−1, which will greatly accelerate the RISC process. In addition, the multiple coupling routes of zero-field splitting (ZFS) interaction can provide energetically nearby lying states, to speed up the RISC pathway, and restrict the phosphorescence decay rate. A smaller ZFS D-tensor of 0.143 cm−1, E/D ≈ 0.094 ≪ 1/3, and Δg > 0 are obtained, indicating that the excited singlet states are hardly mixed into the T1 state; thus, a lower phosphorescence decay rate (kph = 9.29 × 104 s−1) is expected to occur, and the T1 state has a long lifetime, which is helpful for the occurrence of the RISC process. These works are in excellent agreement with the experimental observation and are useful for improving and designing efficient TADF materials.

1. INTRODUCTION

Currently, organic light-emitting diodes (OLEDs) are widely used in high-end smartphones, high-resolution TVs, solid-state lighting, and other fields due to their advantages of high contrast, ultrathin nature, flexibility, high efficiency, nontoxic nature, and so on, and the market scale is still further expanding.1−4 The key to the rapid improvement of OLED performance is the upgradation of luminescent materials. However, the exciton is produced in the ratio of the singlet state to the triplet of 1:3 according to the spin-statistical quantum mechanism during the charge recombination processes; thus, the internal quantum efficiency (IQE) of the triplet exciton for the transition forbidden decay is limited to 75% (see Figure 1).4 Therefore, how to realize 100% IQE by efficiently harvesting triplet excitons has become a hot issue and difficult topic in the OLED field in recent 30 years, and searching for a new generation of OLED materials has become the main focus of scientists’ research.5−7

Recent studies have found that some compounds, such as low-cost and environmentally friendly Cu(I) complexes, as well as with purely organic molecules,5−7 display thermally activated delayed fluorescence (TADF) in OLEDs and can harvest all excitons and achieve nearly 100% IQE (Figure 1).

Consequently, the TADF molecule as a candidate material of the third-generation OLEDs has also attracted much attention. In TADF emitters, a fast reverse intersystem crossing (RISC) process from a triplet (T1) to a singlet manifold (S1) with the help of thermal energy at room temperature is the key to the efficient utilization of triplet excitons.4,9 However, RISC is a spin-forbidden process, and the spin-flipping rate as the necessary condition to harvest the nonradiative T1 state into radiative S1 in TADF molecules is generally low, which greatly limits its application in OLEDs.10,11 Many researchers are devoted to resolving this thorny issue.10−12 We know that the spin-flipping process is traditionally described by the mixing of the singlet and triplet wave functions, and the mixing degree (γ) of these states can be expressed as the relationship γ ∝ SOC(S1−T1)/ΔE(S1−T1), where SOC(S1−T1) is the spin–orbit coupling (SOC) value.
between the $S_1$ and $T_1$ states and $\Delta E(S_1\rightarrow T_1)$ is their energy gap. According to this relationship, the small $\Delta E(S_1\rightarrow T_1)$ and large SOC($S_1\rightarrow T_1$) values are requirements for achieving efficient RISC.

From the principles of theoretical chemistry, it is relatively easy to obtain molecules with small $\Delta E(S_1\rightarrow T_1)$ by structuring a strong charge-transfer (CT) exciton character for the $S_1$ and $T_1$ states with the help of a covalently linked electron donor–acceptor (D–A)–type unit. Over the past decade, TADF molecules with small $\Delta E(S_1\rightarrow T_1)$ values ($<0.1$ eV) have been reported in a broad series of simple D–A–type molecules.\(^6,7\) In this case, the occurrence of TADF is closely related to the CT $S_1$ and $T_1$ states with the frontier orbitals, namely, the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO), that are spatially well separated. This leads to an extremely small electron–exchange interaction \[\text{equal to } \Delta E(S_1\rightarrow T_1)/2; \text{it is a competitive mechanism to suppress ISC through the process of spin conservation}.\] due to small spatial overlap between the HOMO and LUMO.\(^5\) Until now, the design strategy of efficient TADF molecules still mainly focuses on minimizing the gap of $\Delta E(S_1;T_1)$.

It is generally believed that reducing $\Delta E(S_1;T_1)$ is an essential approach to accelerate the conversion from the $T_1$ to the $S_1$ state for realizing efficient TADF. Nevertheless, in this understanding, the study of TADF is also confronted with the two dilemmas: one is that some compounds having very small $\Delta E(S_1;T_1)$ represent the poor TADF character and other compounds with a large $\Delta E(S_1;T_1)$ of few hundreds of mega-electron-volts have highly efficient TADF, which implies that the $\Delta E(S_1;T_1)$ gap is not the only determining factor for the occurrence of TADF;\(^13\) and the other is that a small $\Delta E(S_1;T_1)$ value with weak exchange interaction between the unpaired electrons requires a small spatial overlap of HOMO and LUMO from the quantum chemical considerations, which results in a weak oscillator strength of the $S_1 \rightarrow S_0$ transition and causes the slow fluorescence rate $k_f$ and low luminescence efficiency. In other words, the corresponding rate $k_f$ and $\Delta E(S_1;T_1)$ are strongly correlated and suppress each other.

Another disadvantage of this strategy in minimizing the $\Delta E(S_1;T_1)$ gap is that the SOC between the $S_1$ and $T_1$ states having the same electronic configuration is strictly forbidden because the spin flipping needs to be balanced by the variation of the orbital angular momentum to hold the total momentum conservation, leading to a negligibly small SOC interaction between the two pure $^{13}$CT states in the Born–Oppenheimer approximation.\(^14\) This means that the RISC from a CT-type $T_1$ into a CT-type $S_1$ is less efficient, no matter how small the $\Delta E(S_1;T_1)$ is, and the calculation results of this paper also support this conclusion, $k_{\text{RISC}} \approx 10^4$ s\(^{-1}\). The slow RISC process leads to a long $T_1$ exciton lifetime and exciton annihilation, which is a vital reason for the serious roll-off effects and material degradation in OLEDs. In 2019, H. Yersin and his team\(^15,16\) proposed a new design mechanism for the fourth-generation OLEDs; this design strategy is to provide energetically nearby lying states for the emitting $T_1$ state to accelerate the RISC process by their SOC and configuration interaction paths. However, it is known that the radiation rate $k_{\nu}$ from the $T_1$ to the ground state $S_0$ is proportional to the relationship $k_{\nu} \propto \alpha \Delta E(S_0;T_1)^3M_j^3$; here, $\alpha$ is a constant, $\Delta E(S_0;T_1)$ denotes the transition energy, and $M_j$ is the SOC $T_1 \rightarrow S_0$ transition moment and is expressed as follows\(^17\)

$$M_{j\in x,y,z} = \sum_n \frac{(S_0|\mu|S_n)\langle S_n|\hat{H}_{\text{SOC}}|T_1\rangle}{E(T_1) - E(S_n)} + \sum_m \frac{(T_1|\mu|T_m)\langle T_m|\hat{H}_{\text{SOC}}|S_0\rangle}{E(T_m) - E(S_0)}$$

where $\mu$ represents a projection of the dipole moment operator on the $j$-axis and $\hat{H}_{\text{SOC}}$ is the SOC operator. Based on this relationship, the introduction of strong $\langle S_n|\hat{H}_{\text{SOC}}|T_1\rangle$ or $\langle T_1|\hat{H}_{\text{SOC}}|T_1\rangle$ interaction paths can not only accelerate the RISC process but also increase the $k_{\nu}$ rate. Consequently, it is also a challenge to achieve a rational balance between a strong SOC interaction among nearby low-energy excited states and the $k_{\nu}$ rate in designing new TADF molecules.

Based on the above description, in the face of these contradictions and challenges, Yersin and co-workers have experimentally designed and synthesized an Ag(I)-based TADF complex with Ag(dpdb)(P\(_2\)-nCB)[dpdb = 2,9-di-n-butyl-1,10-phenanthroline and P\(_2\)-nCB = nido-carborane-bis(diphenylphosphine)]\(^18,19\) with the help of theoretical ideas of high-transition-rate $k_{\nu}$ small $\Delta E(S_1;T_1)$, and structural rigidity to decrease the nonradiative relaxation rate of the excited state (structure shown in Figure 2). It is shown that Ag(dpdb)(P\(_2\)-nCB) displays a 100% emission quantum yield.
and ultrashort radiation TADF decay time, which is evidently shorter than that of any other TADF materials reported so far.

In contrast to the experimental investigation, the theoretical exploration of the design strategy for the Ag-based TADF complex seems to be extremely backward. However, as an indispensable tool to reveal the nature of the experiment, accurate theoretical calculation can not only provide a quantitative understanding of the photophysical process of the TADF molecule but also possibly trace back to the origin of the experimental results. As mentioned earlier, to provide a new strategy for designing TADF materials, it is essential to fully understand the three correlated processes of two radiations (S₀ → S₁ and T₁ → S₀) and one nonradiation of T₁ → S₁. In the current article, we first quantitatively calculated the emission rates and spectra for the Ag(dbp)(P₂-FnCB) complex by employing the Fermi golden rule combination of time-dependent density functional theory (TD-DFT) and the path integral approach to dynamics,2⁰ in which they account for temperature effects, vibronic coupling, and the Duschinsky rotation between modes. Here, the vibronic SOC effects are also considered to calculate the RISC rate relative to the normal-mode coordinate, which is similar to the classical Herzberg–Teller (HT) effect of the dipole transition. Moreover, the contributions of the zero-order Frank–Condon (FC) approximation and the first-order HT effect to radiative rates and spectra are also quantitatively analyzed separately. On the basis of these quantitative analyses, we will refine the theoretical ideas of TADF molecular design in order to provide theoretical supports and new ideas for new design concepts in the future.

2. COMPUTATIONAL DETAILS

Geometry and Electronic Structure Calculations. The version of the ORCA 4.2.1 program package2¹ was used to perform all calculations. Geometry optimizations were carried out by employing the BP86 functional together with the resolution of the identity (RI) approximation.²²,²³ The BP86 functional was chosen because it provides excellent optimized geometries and a typical accuracy of the vibrational frequencies containing metal complexes. All atoms were first described by the def2-SVP basis set in conjunction with the def2/J and the def2-SVP/C auxiliary basis sets required for the RI approximation.²⁴ The Becke–Johnson (BJ) damping parameters were also used in Grimme’s D3 dispersion correction, writing D3BJ²⁵,²⁶ Then, the effective core potential (ECP) of de2-ECP was considered to be recalculated for the metal Ag.²⁷

In the optimization, we set tight convergence criteria (TightSCF and TightOPT) and increased the integration grids (Grid5 and GridXS), and all the other parameters were chosen as default, unless otherwise specified. Numerical frequency calculations were computed using the same functional and basis set to verify the optimized structures to be the local minima on the potential energy surface. The geometry coordinates are shown in Table S1 of the Supporting Information. The optimized ground-state geometry is found to be well consistent with the experimental X-ray geometry (Tables S2 and S3).¹⁸

In the calculation of excited-state properties, the traditional DFT may fail completely to predict the properties of the CT excited-state system, which is due to the improper exchange correction approximation and the incorrect behavior at asymptotically large distances.³⁸ Among the DFT functions, the range-separated hybrid functional is the most satisfactory method to describe the CT states and has become a tool of choice to study the excited states of such TADF materials when the range-separation parameter is optimally tuned.²⁹ Therefore, the ωB97X-D3 functional is used to deal with the excited-state properties in the text, and in addition, it is supplemented by the most popular hybrid functional B3LYP calculation. The range-separation parameter ω value is strongly dependent on the studied systems, and ω was tuned by minimizing the target expression ²⁹

\[
j^2 = \sum_{i=0}^{1} (\epsilon_i(N + i) + IP(N + i))^2
\]

where IP and \(\epsilon_i\) indicate the vertical first ionization potential and the HOMO energy of the molecule, respectively. The optimal tuning of ω was performed by using the tuning optDFTw procedure²⁰ and expressed as \(\omega^*\)B97X-D3.

In the Ag(dbp)(P₂-FnCB) complex, relativistic effects should be expected, and the scalar relativistic effects were treated by the second-order Douglas–Kroll–Hess (DKH2) method.³¹ Electronic vertical absorption and emission were thus simulated using the \(\omega^*\)B97X-D3 and B3LYP functionals in conjunction with the large scalar relativistically recontructed DKH-def2-TZVP-f basis set (old-DKH-TZVP for the Ag atom) and the matching auxiliary basis set of SARC/J.²⁴,³² The RIJCOSX algorithm is also used to accelerate the calculation of the Coulomb and Hartree–Fock exchange integrals in these hybrid functionals.³³ Solvation effects were taken into account by employing the conductor-like polarizable continuum model (CPCM), and toluene (\(\epsilon = 9.08\)) was selected as the solvent,³⁴ which is consistent with the experiment. In this case, the optimal \(\omega^*\) value in the \(\omega^*\)B97X-D3 is calculated to be 0.0102 Bohr⁻¹. The SOC effects along with the Zeeman interactions are obtained from TD-B3LYP or TD-\(\omega^*\)B97X-D3 using the quasi-degenerate perturbation theory (QDPT) approach,³⁵ where an accurate multicenter spin–orbit mean-field (SOMF) method of the Breit–Pauli SOC operator⁶ at all centers leads to a mixing of different multiplicities (\(\Delta S = 0, \pm 1\)).

Excited-State Dynamics and Spectral Calculation. The dynamic characteristics of excited states, such as fluorescence and phosphorescence rates corresponding to the spectra between an initial state \(i\) and a final state \(f\), are obtained by using Fermi’s golden rule³⁷ from quantum electrodynamics combined with the path integration approach (a more detailed description is given in ref 20), which can be expressed as follows²⁰,³⁸

\[
k(\omega) = \frac{2\omega}{3\epsilon} \sum_{if} \sum_{\Theta} \frac{\epsilon_i}{\epsilon_f} \langle \Theta \mid \mu(\Theta) \rangle \langle \Theta \mid \mu(\Theta) \rangle \int \epsilon(E_i - E_f - \omega) d\omega
\]

where \(\mu\) is the dipole operator, \(\Theta = 0\) is the vibrational wavefunction of the initial \(i\) or final \(f\) state, and \(\epsilon_i\) is the total vibrational energy; \(\epsilon - \frac{\omega}{\omega} Z\) indicates the Boltzmann population at temperature \(T\), and \(Z\) is the partition function written as

\[
Z = \sum_i \frac{\epsilon_i}{\exp(\epsilon_i/kT)}
\]

here, the electronic part of the transition dipole that varies with nuclear displacements is taken into account for emission rates and spectra, and the matrix elements of \(\mu\) relative to the nuclear coordinates \(Q_i\) can be expanded as
In formula 5, the zero-order term is the FC approximation by keeping only the coordinate independence, and for the second term, only the first-order contribution is considered in the vibration coupling or the so-called HT effect. Note that the expanded transition dipole always chooses the nuclear coordinates of the final state, and all spectra were normalized to one.

The intersystem crossing rates from a given initial state $i$ to a final state $f$ can be also calculated by Fermi’s golden rule, which means that the vibrational and electronic contributions to the ISC and RISC rates can be separated. The dependence of temperature, which is particularly critical for the RISC rates, is introduced through a Boltzmann population of the vibrational $\Theta_i$ level in the $i$ state. In such a case, the ISC rate may be expressed as

$$\mu(Q) = \mu_0 + \sum_i \frac{\partial \mu}{\partial Q_i} \bigg|_{Q_i=0} Q_i + \cdots$$

(5)

In formula 5, the zero-order term is the FC approximation by keeping only the coordinate independence, and for the second term, only the first-order contribution is considered in the vibration coupling or the so-called HT effect. Note that the expanded transition dipole always chooses the nuclear coordinates of the final state, and all spectra were normalized to one.

The intersystem crossing rates from a given initial state $i$ to a final state $f$ can be also calculated by Fermi’s golden rule, which means that the vibrational and electronic contributions to the ISC and RISC rates can be separated. The dependence of temperature, which is particularly critical for the RISC rates, is introduced through a Boltzmann population of the vibrational $\Theta_i$ level in the $i$ state. In such a case, the ISC rate may be expressed as

$$k_{ISC} = \frac{2\pi}{\hbar Z} \sum_{i,f} e^{-\frac{\epsilon_f}{kT}} \langle \Phi_i, \Theta_i | \hat{H}_{SOC} | \Phi_f, \Theta_f \rangle^2 \delta(E_i - E_f)$$

(6)

Here, $\hbar$ is the reduced Planck constant, $|\Phi_{i,f}\rangle$ is the orbital wavefunction of the $i$ or $f$ state, and other parameters have the same physical meaning as in eq 3.

As for the coupling contribution of vibration, it is necessary to integrate the electronic and nuclear degrees of freedom. In order to obtain this coupling matrix element in eq 6, it is expanded into a Taylor expansion in the normal coordinates $Q_0$ around the final state as a reference configuration $Q_0 = 0$, see eq 7

$$\langle \Phi_{i}, \Theta_{i}, v | \hat{H}_{SOC} | \Phi_{f}, \Theta_{f}, v \rangle = \langle \Phi_{i} | \hat{H}_{SOC} | \Phi_{f} \rangle_{Q_0=0} (\Theta_{i}, \Theta_{f}, v) + \frac{\partial}{\partial Q_i} \langle \Phi_{i} | \hat{H}_{SOC} | \Phi_{f} \rangle_{Q_0=0} \left(\Theta_{i}, \Theta_{f}, v\right) + \cdots$$

(7)

where the first term on the right side is the so-called FC approximation which ignores the dependence of coupling matrix elements on molecular vibration and also named as the direct SOC term; the second term is very similar to the regular HT processing of the elements of the electronic dipole transition matrix, with significant changes in the ISC rates, and

Figure 3. Drawing UV—vis spectra including SOC correction for the liquid CH2Cl2 phase at the TD-B3LYP (a,b) and TD-ω*B97X-D3 (c,d) levels, taking into account the DKH2 Hamiltonian scalar relativistic calculation combined with the corresponding recontracted DKH-def2-TZVP(-f) basis set (old-DKH-TZVP for Ag)
the first-order derivative of this coupling with respect to the normal-mode coordinate is called vibronic SOC.

These calculations were carried out using the new ESD module of the ORCA program recently developed,\textsuperscript{21} with default settings and Duschinsky mixing.\textsuperscript{40} Moreover, for the sake of speeding up the numerical calculation of the transition dipole moment derivatives, computation is avoided using central differences (labeled CentralDiff = False in ORCA) in all displacements.\textsuperscript{20}

### 3. RESULTS AND DISCUSSION

#### Electronic Structure of the Excited States. Spectral Analysis

The visible spectra of Ag(dbp)(P\textsubscript{2-}CB) were simulated by the TD-\textalpha*97X-D3 and TD-B3LYP methods including SOC correction and using the DKH2 Hamiltonian combined with the corresponding retracted DKH-def2-TZVP(-f) basis set in CH\textsubscript2Cl\textsubscript2 solution. The band structure and combined with the corresponding recontracted DKH-def2-TZVP(-f) including SOC correction and using the DKH2 Hamiltonian simulated by the TD-B3LYP method amount to 99.3%\textsuperscript{a} B3LYP and TD-\textalpha*97X-D3 methods, respectively, indicating that the (S\textsubscript{i}H\textsubscript{SOC}/T\textsubscript{j}) interaction is extremely weak. In Figure 3, the spectrum shows the S\textsubscript{0} → S\textsubscript{1} transition of the stronger spin-allowed band with the maxima at 530.4 (TD-B3LYP) and 523.1 nm (TD-\textalpha*97X-D3), which is found to be in good agreement with the experimental result of 585 nm in dichloromethane (526 nm for powder), and this also shows that the calculation method is relatively reliable. Besides, the calculated energy splitting of ΔE(S\textsubscript{i}−T\textsubscript{j}) from the difference in the vertical excitation energies, is equal to 725 cm\textsuperscript{-1} at the TD-\textalpha*97X-D3/DKH-def2-TZVP(-f) level, which is thus seen to perfectly match the experimental ΔE(S\textsubscript{0}−T\textsubscript{1}) = 650 cm\textsuperscript{-1}.\textsuperscript{18}

#### Excited-State Analysis

The frontier orbitals, electron density difference, and transition density maps of selected excitation states of Ag(dbp)(P\textsubscript{2-}CB) are shown in Figure 4;

#### Table 1. Selected Low-Energy Vertical Transitions (ΔE in eV) with the Corresponding Oscillator Strengths (f), Natural Transition Orbitals, and Character Assignments for Ag(dbp)(P\textsubscript{2-}CB) in the S\textsubscript{0} Optimized Geometry at the B3LYP (and \textalpha*97X-D3)/DKH-def2-TZVP(-f) Theory Level

| state | ΔE (eV) | f | main contribution | character |
|-------|---------|---|-------------------|-----------|
| T\textsubscript{1} | 2.246 | 5.28 × 10\textsuperscript{-7} | H ≥ L (94.4%) | \textsuperscript{3}CT |
| S\textsubscript{1} | 2.338 | 5.87 × 10\textsuperscript{-2} | H ≥ L (99.3%) | \textsuperscript{3}CT |
| S\textsubscript{2} | 2.438 | 8.87 × 10\textsuperscript{-3} | H ≥ L+1 (98.9%) | \textsuperscript{3}CT |
| T\textsubscript{2} | 2.518 | 2.17 × 10\textsuperscript{-5} | H ≥ L+1 (54.5%), H-3 ≥ L+1 (29.7%) | \textsuperscript{3}CT |
| S\textsubscript{3} | 2.606 | 2.14 × 10\textsuperscript{-4} | H ≥ L (99.0%) | \textsuperscript{3}CT |
| T\textsubscript{3} | 2.846 | 3.30 × 10\textsuperscript{-6} | H ≥ L+1 (42.9%), H-3 ≥ L+1 (32.7%), H-7 ≥ L (6.3%) | \textsuperscript{3}CT |
| T\textsubscript{4} | 3.163 | 2.32 × 10\textsuperscript{-6} | H ≥ L+2 (74.9%), H ≥ L+2 (5.3%) | \textsuperscript{3}CT |
| T\textsubscript{5} | 3.185 | 3.13 × 10\textsuperscript{-6} | H ≥ L+2 (47.3%), H ≥ L+3 (11.6%), H-3 ≥ L (7.8%) | \textsuperscript{3}CT |

\textsuperscript{3}CT = charge-transfer state. \textsuperscript{b}The highest occupied orbital and the lowest unoccupied orbital are abbreviated as H and L. For example, H-1 is then accordingly the orbital below the HOMO; the percentage in brackets indicates the contribution of the corresponding orbital transition.

see more details in Figures S1–S4 in the Supporting Information. Calculations reveal that the lowest electronic transitions, corresponding to the states S\textsubscript{1} and T\textsubscript{1}, with the orbital energy in eV, excitation energy ΔE (in eV), transition density difference, and transition density of Ag(dbp)(P\textsubscript{2-}CB) for T\textsubscript{1}, S\textsubscript{1}, S\textsubscript{2}, and T\textsubscript{2} states calculated at the TD-\textalpha*97X-D3/DKH-def2-TZVP(-f) (\textalpha* = 0.0102) levels including the scalar relativistic DKH2 Hamiltonian calculation in solution.
Ag(dbp)(P2-nCB) restrained this flattening distortion within the reasonable error of ORCA_ESD module calculation.\(^1\) We know that the electron density difference shows the depletion and accumulation of electron density in the process of electron transition, and the coffee color indicates the region of increased electron density in the excited state, whereas purplish-red regions are those of reduced electron density, see Figure 4, and the significant transition density difference is further found between the electron donars of the silver and phosphorus atoms and the acceptor of the dbp ligand; thus, the further found between the electron donors of the silver and the acceptor of the dbp ligand; thus, the electron density difference shows the depletion and accumulation of electron density in the process of electron transition, and the coffee color indicates the region of increased electron density in the excited state, whereas purplish-red regions are those of reduced electron density, see Figure 4, and the significant transition density difference is further found between the electron donors of the silver and phosphorus atoms and the acceptor of the dbp ligand; thus, the further found between the electron donors of the silver and the acceptor of the dbp ligand.

Figure 5. Simulated fluorescence spectra of Ag(dbp)(P2-nCB) at T = 300 K at the B3LYP/def2-TZVP(Δ)//def2/J level for dichloromethane. (a) shows the contribution of the FCHT and FC effects and (b) shows the vibrational resolution spectrum.

\[
\mu_{HL} = e \int \Phi_{\text{HOMO}}(r)^2 \Phi_{\text{LUMO}}(r) dr^3 = e \int \rho_{HL}(r) dr^3 \quad (8)
\]

\[
\rho_{HL}(r) = \Phi_{\text{HOMO}}(r) \Phi_{\text{LUMO}}(r) \quad (9)
\]

where \(\rho_{HL}\) denotes the transition density for the \(S_1\) state. From the above equation, the \(\mu_{HL}\) increases with the increase of the \(\rho_{HL}\) value, namely, when \(\rho_{HL}\) is distributed in the regions that are far away from the coordinate origin. The calculated transition density is outlined in detail in Figure 4; \(\rho_{HL}\) is distributed on the silver and phosphorus atoms and extends over the dbp ligand core that is distant from the origin of the coordinates for the \(S_1\) state, leading to a relatively larger \(\mu_{HL}\) and a larger \(f\), which are beneficial to the fluorescence decay.

On the contrary, the stronger fluorescence may not be conducive to the occurrence of TADF. We know that a key requisite for the TADF occurrence is very small \(\Delta E(S_{1}\rightarrow T_{1})\) with the help of thermal energy, while \(\Delta E(S_{1}\rightarrow T_{1})\) is well approximated by the exchange integral with the HOMO (\(\Phi_{\text{HOMO}}\)) and LUMO (\(\Phi_{\text{LUMO}}\)) for the \(S_1\) and \(T_1\) states, and it can also be estimated by the transition density \(\rho_{HL}\) from the HOMO to LUMO.\(^2\) A smaller \(\Delta E(S_{1}\rightarrow T_{1})\) necessarily requires a smaller transition density \(\rho_{HL}\) which can be described visually by the overlapping integral \(S_{HL}\) of the HOMO and LUMO, see eq 10, and \(S_{HL}\) should have a larger distribution at the intersection of the HOMO and LUMO (see Figure 4).

\[
S_{HL}(r) = \int |\Phi_{\text{HOMO}}(r)||\Phi_{\text{LUMO}}(r)| dr^3 \quad (10)
\]

In this work, the relatively larger \(f = 0.0587\) (TD-B3LYP) of the \(S_0 \rightarrow S_1\) transition (or \(\mu_{HL}\)) appropriately matches with the smaller \(\Delta E(S_{1}\rightarrow T_{1})\) = 725 cm\(^{-1}\), leading to the successful occurrence of TADF.

Fluorescence and Vibronic Coupling. The simulated vibrational fluorescence spectra of Ag(dbp)(P2-nCB) at T = 300 K, taking into account the HT contribution, are depicted in Figure 5, and it can be clearly found that the rigidity of Ag(dbp)(P2-nCB) prevents the distortion of the molecule, where the mode mixing is small, the HT correction only accounts for 15.27% so that the FC approximation is suitable for the study of the fluorescence spectrum. However, the inclusion HT contribution satisfactorily reproduced the overall
trend of the band shape, while the peak band position is less accurate, and a red shift of about 50 nm compared with the experimental value of 585 nm in dichloromethane is observed.

In the same way, compared to the FC calculation ($k_f = 1.79 \times 10^7 \text{ s}^{-1}$), inclusion of the HT effect can enhance the decay rate of fluorescence $k_f$ by about 15.27% at $T = 300 \text{ K}$ and $k_f = 2.11 \times 10^7 \text{ s}^{-1}$ (see Table 2), perfectly matching the experimental value of $k_f = 5.6 \times 10^7 \text{ s}^{-1}$. At a low temperature of 77 K, this HT effect is reduced to 14.31%.

In order to deeply understand the details of the HT effect, eq 5 can be further extended as follows

$$\mu(Q) = \mu_0 \prod_\alpha \langle m_{\alpha} | \alpha \rangle + \sum_i \frac{\partial \mu}{\partial Q_i} \prod_{Q=0} \langle m_{\alpha} | 0 \rangle \prod_{\alpha \neq \beta} \langle m_{\beta} | 0 \rangle + \cdots$$

(11)

herein, $\partial \mu/\partial Q_i$ is the first derivative of the transition dipole moment with respect to the nuclear coordinate of the normal mode $Q_i$. $\langle m_{\alpha} | Q_i \rangle$ indicates the vibration transition dipole moment; $m_\alpha$ and $n_\alpha$ are the vibration quantum numbers; $\langle m_{\alpha} | 0 \rangle$ is the overlap integral using the expression of $Q_i$. The obtained $\partial \mu / \partial Q_i$ and $\langle m_{\alpha} | Q_i \rangle$ are depicted in Figures 6 and 7 and Table S4. As seen in Figure 6, the normal modes with $\omega_{271} = 1499.88 \text{ cm}^{-1}$ and $\omega_{274} = 1583.52 \text{ cm}^{-1}$ make remarkable contributions to $\partial \mu / \partial Q_i$ along all three directions (the z direction is not plotted). The two modes mainly originate from the asymmetric stretchings of the C−C and C−P bonds and bending vibrations of $\angle$C−C−H on the dbp ring. These vibration modes may produce the most intense 0−1 lines at 631.7 nm, which are in perfect agreement with the fluorescence data. The contribution from the normal modes of 1300 to 1650 cm$^{-1}$ would have a slight influence on the line shape of the fluorescence spectrum.

### Table 2. Simulated FCHT and FC Fluorescence ($k_f$ in s$^{-1}$) and Phosphorescent ($k_p$ in s$^{-1}$) Rates of Ag(dbp)(P2-nCB) in Different Environments; Comparison with Published Experimental Data

| temp. (K) | vacuum | solution CH$_2$Cl$_2$ |
|----------|---------|------------------------|
|          | only FC | with FCHT$^{a}$ | only FC | with FCHT$^{a}$ |
|          | $k_f$ | $k_p$ | $k_f$ | $k_p$ | $k_f$ | $k_p$ |
| 77       | $9.31 \times 10^6$ | $5.20 \times 10^{-1}$ | $1.08 \times 10^7$ | $2.47 \times 10^9$ | $1.89 \times 10^7$ | $1.06 \times 10^9$ |
|          | 14.31% | 96.78% | 15.27% | 97.66% | 15.27% | 93.21% |
| 300      | $8.81 \times 10^6$ | $4.66 \times 10^{-1}$ | $1.04 \times 10^7$ | $3.06 \times 10^9$ | $1.79 \times 10^7$ | $6.21 \times 10^9$ |
|          | 14.31% | 96.78% | 14.31% | 96.78% | 14.31% | 96.78% |
| exp. data$^{b}$ | | | | | $5.6 \times 10^7$ (300 K) | $6.7 \times 10^2$ (77 K) |

$^{a}$FC approximation and incorporation of the HT effect. $^{b}$x % denotes the contribution of HT to the rate. $^{c}$Ref 18.
In addition, the FC emission intensity (the first term in equation 11) is proportional to the FC factor and can be evaluated as

$$FC_{S\leftrightarrow S_0} = \frac{S_n}{n_s^4}$$

where $S_n$ represents the Huang–Rhys factor, which can reflect the vibronic coupling strength. On the basis of eq 12, the FC factor is directly proportional to the Huang–Rhys factor with $n_s > 0$ when the $S_n$ is lower than 1.0. The peak intensity is directly decided by the $S_n$ factor, but the strongest FC strength should be the position of $n_s = 0$. As can be seen in Figure 8, all modes, such as $\omega_{382}$, $\omega_{282}$, and so forth, have larger $S_n$ factors, indicating the larger displacement; simultaneously, the $\partial \mu / \partial Q_i$ derivations are very small, which provides a weak vibronic line intensity (Figure 6). The high-frequency normal modes (~1500 cm\(^{-1}\)) are the main contributions to the low-energy emission peaks and have larger reorganization energies, showing the extent of vibronic coupling between the two electronic states, see Figure 8, $\omega_{191} = 1056.11$ cm\(^{-1}\), $S_{191} = 0.22$ and $\omega_{282} = 1632.36$ cm\(^{-1}\), $S_{282} = 0.23$. These vibrations come from the stretchings of the C–C and C–P bonds on the ring of the dbp ligand. To put it in another way, the Huang–Rhys factor is derived from the natural frequency difference of the two structures, and the material has thus sufficient fluorescence stability.

**Spin Mixing and Reverse Intersystem Crossing.** It is generally accepted that reducing $\Delta E(S_1 \rightarrow T_1)$ is an essential approach to promote RISC from the $T_1$ to $S_1$ state for an efficient TADF. However, the opposite examples of efficient TADF complexes with the larger $\Delta E(S_1 \rightarrow T_1)$ have shown that $\Delta E(S_1 \rightarrow T_1)$ is not the only determining factor of efficient TADF. Indeed, theoretical research reveals that only when there is an internal magnetic interaction such as SOC inducing spin mixing between the singlet and triplet states, the RISC depending on $\Delta E(S_1 \rightarrow T_1)$ can be verified to generate TADF. Also, the spin-mixing parameter, $\gamma$, can be simply written as $\gamma^2 = \xi^2/\Delta^2$, which is the sum of the orbital mixing and spin mixing; herein, $\xi$ is the SOC strength and $\Delta$ is the energy difference between the two states. Besides, the ratio between the spin-flip rate to the spin-conserving one is estimated by $\gamma^2 = 4/3\gamma^2$, and all calculated values along the optimized $T_1$ step (see Figure S5) are shown in Table 3 and Figure 9. In calculations, we observe that Ag(dbp)(P2-3nCB) was found to have a very small spin-mixing $\gamma^2$ and spin-flip rate $\gamma^2$, lying within a range of ~10\(^{-5}\) and ~10\(^{-6}\) respectively. As stated above, the $\gamma^2$ is proportional to the SOC strength $\xi^2$, while the direct SOC between the $S_1$ and $T_1$ states is totally forbidden, that is, $\langle 1^{1}CT(S_1)|H_{SOC}|1^{1}CT(T_1) \rangle$ falls to zero (Figure 9, detailed data seen in Tables S5 and S6 of the Supporting Information), leading to a small $\gamma^2$. Even if the SOC effect of the $T_2$ state increases slightly, the energy difference increases sharply, which also gives rise to the small spin-mixing and spin-flip rate. On the spin admixture, no large variation is observed along the optimized $T_1$ step in the RISC process, which shows that the orbital configurations have not changed greatly.

![Figure 8](image-url) Calculated reorganization energies (a) and Huang–Rhys factors (b) vs the normal-mode frequencies during the $S_1 \rightarrow S_0$ process; vibration modes of the largest reorganization energy were inserted into the picture for the $S_1$ state.

Our calculated $k_{RISC}$ and $k_{ISC}$ rate constants are given in Table 4, including the HT and Duschinsky mixing effects. As seen in Table 4, interestingly, the $k_{RISC}$ mainly increased by 2 orders of magnitude, while the $k_{ISC}$ hardly changed when the temperature increased from 77 to 300 K. That is to say, the rate of $k_{RISC}$ is more susceptible to temperature than that of $k_{ISC}$ and it is mainly attributed to the failure to satisfy the conservation of energy with $\Delta E(S_1 \rightarrow T_1) < 0$. At 300 K, the $k_{RISC}$ constant of $T_1 \rightarrow S_1$ is estimated to be $1.72 \times 10^8$ s\(^{-1}\), which is far more than the ISC rate $k_{ISC}$ of 7.28 $\times 10^4$ s\(^{-1}\) in CH$_2$Cl$_2$ solution. Meanwhile, the phosphorescence $k_{RISC}$ rate value is expected to be very small as $9.29\times10^3$ s\(^{-1}\) owing to the smaller SOC and larger energy difference. In such a situation, the $k_{RISC}$ is more favorable to compete with these rates at room temperature, therefore the $S_1$ state can be repopulated from the $T_1$ state by the RISC pathway, and delayed fluorescence possibly occurs.

What is more, we also noted that the vibrational SOC interaction (HT effect) makes a great contribution to $k_{RISC}$ at
Taking into Account the HT Effect

The S1 and T1,2 states in the T1 structure for Ag(dbp)(P2-πCB)

Table 3. Calculated Intersystem Crossing ($\chi^2$) and Spin-Flip ($\chi'$) along the Optimized T1 Step from the S1 Geometry

| optimization steps | $\chi^2$(S1-T1) | $\chi^2$(S1-T2) | $\chi'$(S1-T1) | $\chi'$(S1-T2) |
|--------------------|----------------|----------------|----------------|----------------|
| 1st                | 2.35 x 10^{-3} | 1.02 x 10^{-6} | 3.13 x 10^{-5} | 1.36 x 10^{-6} |
| 5th                | 2.28 x 10^{-3} | 1.08 x 10^{-6} | 3.05 x 10^{-5} | 1.44 x 10^{-6} |
| 13th               | 2.26 x 10^{-3} | 1.08 x 10^{-6} | 3.01 x 10^{-5} | 1.44 x 10^{-6} |
| 19th               | 2.11 x 10^{-3} | 1.06 x 10^{-6} | 2.81 x 10^{-5} | 1.43 x 10^{-6} |
| 24th               | 2.01 x 10^{-3} | 1.05 x 10^{-6} | 2.67 x 10^{-5} | 1.39 x 10^{-6} |
| 28th               | 2.05 x 10^{-3} | 1.04 x 10^{-6} | 2.73 x 10^{-5} | 1.38 x 10^{-6} |
| 33rd               | 2.13 x 10^{-3} | 1.03 x 10^{-6} | 2.84 x 10^{-5} | 1.38 x 10^{-6} |
| $\omega$-B97X-D3   |                |                |                |                |
| 1st                | 4.13 x 10^{-5} | 1.11 x 10^{-6} | 5.51 x 10^{-5} | 1.48 x 10^{-6} |
| 5th                | 4.48 x 10^{-5} | 1.17 x 10^{-6} | 5.97 x 10^{-5} | 1.56 x 10^{-6} |
| 13th               | 4.52 x 10^{-5} | 1.18 x 10^{-6} | 6.03 x 10^{-5} | 1.57 x 10^{-6} |
| 19th               | 4.19 x 10^{-5} | 1.18 x 10^{-6} | 5.58 x 10^{-5} | 1.57 x 10^{-6} |
| 24th               | 4.14 x 10^{-5} | 1.15 x 10^{-6} | 5.52 x 10^{-5} | 1.54 x 10^{-6} |
| 28th               | 4.24 x 10^{-5} | 1.14 x 10^{-6} | 5.65 x 10^{-5} | 1.52 x 10^{-6} |
| 33rd               | 4.19 x 10^{-5} | 1.14 x 10^{-6} | 5.59 x 10^{-5} | 1.52 x 10^{-6} |

Figure 9. Calculated spin–orbital coupling matrix elements between the S1 and T1,2 states in the T1 structure for Ag(dbp)(P2-πCB) at the TD-B3LYP and TD-$\omega$-B97X-D3/DKH-def2-TZVP(-f)//SARC/J levels.

Table 4. Calculated Intersystem Crossing ($k_{ISC}$ for S1 $\rightarrow$ T1) and Reverse Intersystem Crossing ($k_{RISC}$ for T1 $\rightarrow$ S1) Rates Taking into Account the HT Effect of Ag(dbp)(P2-πCB); All Units in s^{-1}; $k_{ISC}^{0}$ for the T1 $\rightarrow$ S0 Crossing Rate

| temp.(K) | $k_{ISC}$ | $k_{RISC}$ | $k_{ISC}^{0}$ | $k_{RISC}^{0}$ |
|----------|-----------|------------|---------------|---------------|
| vacuum only FC |          |            |               |               |
| 77       | 7.63 x 10^4 | 4.67 x 10^4 | 9.50 x 10^3  | 1.93 x 10^3   |
| 300      | 5.83 x 10^5 | 1.52 x 10^4 | 1.51 x 10^3  | 3.06 x 10^3   |

| temp.(K) | $k_{ISC}$ | $k_{RISC}$ | $k_{ISC}^{0}$ | $k_{RISC}^{0}$ |
|----------|-----------|------------|---------------|---------------|
| solution CH2Cl2 only FC |          |            |               |               |
| 77       | 1.38 x 10^4 | 1.54 x 10^4 | 1.29 x 10^4  | 6.28 x 10^4   |
| 300      | 6.83 x 10^5 | 3.07 x 10^5 | 7.28 x 10^5  | 1.72 x 10^5   |

Table 4. Calculated Intersystem Crossing ($k_{ISC}$ for S1 $\rightarrow$ T1) and Reverse Intersystem Crossing ($k_{RISC}$ for T1 $\rightarrow$ S1) Rates Taking into Account the HT Effect of Ag(dbp)(P2-πCB); All Units in s^{-1}; $k_{ISC}^{0}$ for the T1 $\rightarrow$ S0 Crossing Rate

| temp.(K) | $k_{ISC}$ | $k_{RISC}$ | $k_{ISC}^{0}$ | $k_{RISC}^{0}$ |
|----------|-----------|------------|---------------|---------------|
| 77       | 1.38 x 10^4 | 1.54 x 10^4 | 1.29 x 10^4  | 6.28 x 10^4   |
| 300      | 6.83 x 10^5 | 3.07 x 10^5 | 7.28 x 10^5  | 1.72 x 10^5   |

$^{5}$FC approximation and incorporating the HT effect. $^{6}$x % denotes the contribution of HT to the rate.

300 K, accounting for 89.88% of the total rate while only 65.55% for the $k_{ISC}$ in solution, which further indicates that the HT effect plays a vital role in improving RISC conversion. To deeply explore the vibrational SOC effect, we calculated the relationship between $\langle S_{1}|H_{SOC}|T_{1} \rangle$ and $Q_{2}$, as shown in Figure 10. The involvement of the normal modes with low-frequency vibrations (<1600 cm^{-1}) can be quantitatively observed by calculating the derivatives of these individual modes, leading to a tremendous increase of the SOC interaction. The average value (red line) of $\partial\langle S_{1}|H_{SOC}|T_{1} \rangle/\partial Q_{2}$ for the RISC T1 $\rightarrow$ S1 process is 1 order of magnitude higher than that of $\partial\langle S_{1}|H_{SOC}|T_{1} \rangle/\partial Q_{2}$ (black) for the ISC process in the CH2Cl2 solution. These results indicate that the S1 state may be directly populated and lead to delayed fluorescence in solution.

Phosphorescence and Zero-Field Splitting. As eq 1 described above, the phosphorescence rate $k_{\phi}$ is proportional to the spin–orbit-coupled T1 $\rightarrow$ S0 transition moment M in the case of the invariant $\Delta E(T_{1}-S_{0})$ gap. Thus, the higher-lying states have to be considered because they can mix into the emitting triplet state via direct or indirect SOC, which divides the T1 manifold into three energy-separated sublevels in the absence of an external field. This splitting is called as zero-field splitting, and it is normally measured as the D-tensor.44 Furthermore, the spin and orbital angular momenta interact with an external magnetic field, leading to the Zeeman interaction characterized by the g-factor, which can be used as a measure of the effective SOC. The distinction between the

$^{5}$FC approximation and incorporating the HT effect. $^{6}$x % denotes the contribution of HT to the rate.
Quasi-Restricted Orbital (QRO) Approach in the CPCM (CH2Cl2) for Ag(dbp)(P2-)

the same spin excited states but also from different spin excited states.45

The data in parentheses represents the total value of the first derivatives of SOC.

two tensors (D-tensor and g-factor) is that only the excited states with the same total spin as the T1 state contribute to the g-factor, whereas the D-tensor contains terms not only from the same spin excited states but also from different spin excited states.

The calculated parameters of the g-factor and D-tensor using the ωB97X-D3/B3LYP methods and the individual contributions are exhibited in Table 5, and some vital excitation analysis of the contributions can be seen in Figure 11. As shown, the D parameters are very small, that is, 0.13719 and 0.14265 cm⁻¹ at the B3LYP and ωB97X-D3 levels, respectively; the E/D value is smaller and far less than 1/3, which means that the excited states are hardly mixed into the T1 state. In order to further explore the contribution origins of the D-tensor, the SOC contribution is decomposed into different types of excitations. It is found that the larger contribution of SOC to the D-tensor mainly comes from the excitations of spin-allowed T1 → Tm transitions. The spin-pairing (i.e., triplet → singlet) excitations are minimal, accounting for about 0.04% of the D-tensor at the ωB97X-D3 level, which implies that the excited singlet states can hardly be mixed into the T1 state by the SOC interactions, leading to a smaller T1 → S0 transition moment Mₑ as expected, and it is helpful for the occurrence of the RISC process.

The g-shift (Δg), as a measure for effective SOC, is also given in Table 5 and Figure 11. According to the formulation proposed by F. Neese, Δg can be decomposed as follows46

\[ g = g_a + \Delta g = g_a + \Delta g_{\text{RMC}} + \Delta g_{\text{DSO}} + \Delta g_{\text{PSO}} \]  

where \( g_a \) is equal to 2.0023193, \( \Delta g_{\text{RMC}} \) denotes a relativistic mass correction, \( \Delta g_{\text{DSO}} \) is a diamagnetic spin–orbit correction, and \( \Delta g_{\text{PSO}} \) is the orbital Zeeman and SOC cross-term, termed \( \Delta g_{\text{OZ/SOC}} \). It can be seen in Table 5 that \( \Delta g \) virtually depends on the third term, \( \Delta g_{\text{PSO}} \), while \( \Delta g_{\text{RMC}} \), like other relativistic effects, is negligibly small in Ag(dbp)(P2-nCB). The second

![Figure 10](https://doi.org/10.1021/acsomega.2c00036)

**Figure 10.** First derivatives of SOC with respect to normal-mode coordinate \( Q_n \) between \( S_0 \) and \( T_1 \) based on the HT effect: (a) gas phase and (b) CH2Cl2. The data in parentheses represents the total value of the first derivatives of SOC.

![Figure 11](https://doi.org/10.1021/acsomega.2c00036)

**Figure 11.** Diagram from the vital excitation analysis of the contributions to the individual components of \( \Delta g_{\text{iso}} \) and \( D(\alpha \rightarrow \beta) \) of the T1 state for the Ag(dbp)(P2-nCB) compound.

**Table 5.** Calculated Zero-Field Splitting Tensors (\( D \) and \( E \) in cm⁻¹) and g-Factor Constants of the Triplet-State T1 Using the Quasi-Restricted Orbital (QRO) Approach in the CPCM (CH2Cl2) for Ag(dbp)(P2-nCB)

| method         | contributions | \( D(\alpha \rightarrow \alpha) \) | \( D(\beta \rightarrow \beta) \) | \( D(\alpha \rightarrow \beta) \) | \( \Delta g_{\text{iso}} \) | \( g_{\text{iso}} \) | \( g_{\text{tot}} \) |
|----------------|---------------|------------------------------------|------------------------------------|------------------------------------|------------------------|----------------|----------------|
| B3LYP SOC     | \( \alpha \rightarrow \alpha \) | 0.06431                             | 0.00450                            | 0.00418                            | \( \alpha \rightarrow \beta \) | 0.0001812 | -0.0001812 |
|               | \( \beta \rightarrow \beta \) | 0.08216                             | 0.02089                            | 0.00267                            | \( \alpha \rightarrow \beta \) | 0.00004367 | 0.0003999 |
|               | \( \alpha \rightarrow \beta \) | 0.00005                             | 0.00005                            | 0.000267                           | \( \alpha \rightarrow \beta \) | 0.0002673 | 0.0015798 |
|               | \( \beta \rightarrow \beta \) | 0.03066                             | -0.00986                           | 0.000267                           | \( \alpha \rightarrow \beta \) | 0.00002528 | 0.0017985 |
|               | total         | 0.13719                             | 0.01559                            | 0.0002528                          | \( \alpha \rightarrow \beta \) | 0.0005228 | 0.0030960 |
| ωB97X-D3 SOC  | \( \alpha \rightarrow \alpha \) | 0.06769                             | 0.00135                            | 0.0001812                          | \( \alpha \rightarrow \beta \) | -0.0001830 | -0.0001830 |
|               | \( \beta \rightarrow \beta \) | 0.04105                             | 0.01760                            | 0.000434                           | \( \alpha \rightarrow \beta \) | 0.0000434 | 0.0004408 |
|               | \( \alpha \rightarrow \beta \) | 0.00006                             | 0.00006                            | 0.0002794                          | \( \alpha \rightarrow \beta \) | 0.0002794 | 0.0015817 |
|               | \( \beta \rightarrow \beta \) | 0.03386                             | -0.00568                           | 0.0005228                          | \( \alpha \rightarrow \beta \) | 0.0005228 | 0.0031553 |
|               | total         | 0.14265                             | 0.01334                            | 0.0005228                          | \( \alpha \rightarrow \beta \) | 0.0005228 | 0.0031247 |

\( ^a g_{\text{iso}} = 1/3(g_a + g_\beta + g_\gamma) \) and \( g_\alpha = 2.0023193. ^b \Delta g_{\text{iso}} = 1/3(\Delta g_a + \Delta g_\beta + \Delta g_\gamma). \)
term $\Delta g^{\text{gos}}$ is also relatively small and has an opposite sign for the $\Delta g^{\text{soc}}$ term, nearly canceling.

We know that $\Delta g^{\text{gos}}$ originates from the interaction of the SOC and external magnetic field, and only transitions between the orbital coupling pairs, with a small energy gap and a large coupling interaction, can contribute efficiently to $\Delta g^{\text{gos}}$. Also, the coupling of the different spin space ($\alpha$ and $\beta$ electron) actually leads to different negative and positive contributions to the $\Delta g^{\text{gos}}$ tensor. As shown in Figure 11, the effective coupling involving the vacant $\beta$ spinor, $\langle \psi_{217}\phi_{HOMO}\psi_{2198} \rangle = 9.46 \, \text{cm}^{-1}$, and $\Delta E(\psi_{217}\beta-\psi_{2198}) = 0.824 \, \text{eV}$ produces positive $\Delta g$ $g > 2.0023193$ (see Table 5), that is to say, leading to the deshielding contributions. This indicates that the interaction between metal Ag and the dbp ligand is a weak bond, and this electronic structure inhibits the SOC between different spin states, which makes it possible for TADF to occur.

4. CONCLUSIONS

To date, the design strategy of efficient TADF molecules is still mainly focused on minimizing the gap of $\Delta E(S_i-T_i)$. However, we all know that the $\Delta E(S_i-T_i)$ gap is not the only determining factor for the occurrence of TADF. Thus, it became a challenge to design and develop efficient TADF materials.

Theoretical calculation is an indispensable and powerful method for the investigation and design of new materials. The main purpose of this article is to quantitatively calculate the dependence of TADF efficiency on various parameters of Ag(dbp)(P$_2$-nCB) complex by means of an accurate quantum calculation method combined with the path integral approach to dynamics, which accounts for temperature effects, vibronic coupling, and the Duschinsky rotation between modes. Based on these quantitative analyses, we obtain the results as follows: (i) first, regulating the relationship between the transition dipole moment $\mu_{\text{HL}}$ of $S_0 \rightarrow S_1$ and the energy gap $\Delta E(S_i-T_i)$ of the excited singlet $S_1$ and triplet $T_1$ states because the $\mu_{\text{HL}}$ and $\Delta E(S_i-T_i)$ are approximately proportional to the transition density $\rho_{\text{HL}}$ from the HOMO to LUMO, while they are inversely proportional to each other for efficient TADF. In text, the relatively larger $f = 0.0587$ (TD-B3LYP) of the $S_0 \rightarrow S_1$ transition (or $\mu_{\text{HL}}$) appropriately matches with the smaller $\Delta E(S_i-T_i) = 725 \, \text{cm}^{-1}$, and a relatively small $\Delta E(S_i-T_i)$ is required for efficient TADF materials, leading to the successful occurrence of TADF; (ii) second, regulating the relative sizes of the spin–orbit admixtures between the $T_1$ state and excited singlets, a smaller ZFS D-tensor of 0.143 cm$^{-1}$, $E/D \approx 0.094 \ll 1/3$, and $\Delta g > 0$ are all obtained, indicating that the excited singlet states are hardly mixed into the $T_1$ state, thus, a lower phosphorescence decay rate ($k_p$) is expected to occur, which is helpful for the occurrence of the RISC process. In vacuum, $k_{\text{RISC}} \approx 4.67 \times 10^4 \, \text{s}^{-1} \gg k_p \approx 5.20 \times 10^4 \, \text{s}^{-1}$ for the FC approximation at 77 K; (iii) third, the HT, temperature, and environmental effects must be considered in the nonradiative ISC process, especially $k_{\text{RISC}}$. The calculated results show that the vibrational SOC interaction (HT effect) makes a great contribution to $k_{\text{RISC}}$ at 300 K, accounting for 89.88% of the total rate in solution, and the $k_{\text{RISC}}$ mainly increases by 2 orders of magnitude, while $k_{\text{ISC}}$ hardly changes when the temperature rises from 77 to 300 K, and the $k_{\text{ISC}}$ is estimated to be $1.72 \times 10^8 \, \text{s}^{-1}$, which is far more than the ISC rate $k_{\text{ISC}}$ of 7.28 $\times 10^7 \, \text{s}^{-1}$ in CH$_2$Cl$_2$ solution; (iv) the rigid structure together with the strongly electron-donating negatively charged P$_2$-nCB ligand for Ag(dbp)(P$_2$-nCB) is also one of the design principles.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c00036.

Coordinates of the optimized geometric structure for Ag(dbp)(P$_2$-nCB); comparison of selected geometry parameters of Ag(dbp)(P$_2$-nCB); frontier orbitals, excitation energy $\Delta E$ (in eV), transition density difference and transition density for $T_1$, $S_1$, $S_2$, and $T_2$ states at the TD-B3LYP/DKH-def2-TZVP($f$) level; vital vibrational frequency ($\omega_i$ in cm$^{-1}$), reorganization energy ($\lambda_i$ in cm$^{-1}$), Huang–Rhys factor ($S_i$), and vibrational transition dipole moment integral for the lowest singlet excited state $S_i$; SOC matrix elements between $T_m$ and $S_n$ states; and energy change diagrams of the optimized $S_i$ step from the $T_1$ geometry (PDF).

AUTHOR INFORMATION

Corresponding Author

LingLing Lv — School of Chemical Engineering and Technology, Tianshui Normal University, Tianshui, Gansu 741001, China; Supercomputing Center for Theoretical Chemistry, Tianshui Normal University, Tianshui, GanSu 741001, China; Email: lvling002@163.com, lvling100@163.com

Authors

Kun Yuan — School of Chemical Engineering and Technology, Tianshui Normal University, Tianshui, Gansu 741001, China; Supercomputing Center for Theoretical Chemistry, Tianshui Normal University, Tianshui, GanSu 741001, China

TianYu Zhao — School of Chemical Engineering and Technology, Tianshui Normal University, Tianshui, Gansu 741001, China; Supercomputing Center for Theoretical Chemistry, Tianshui Normal University, Tianshui, GanSu 741001, China

HuiXue Li — School of Chemical Engineering and Technology, Tianshui Normal University, Tianshui, Gansu 741001, China; Supercomputing Center for Theoretical Chemistry, Tianshui Normal University, Tianshui, GanSu 741001, China

YongCheng Wang — College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou, Gansu 730070, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00036

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (grant nos. 21663025 and 22163008). We gratefully thank Dr. Haitao Sun (East China Normal University) for providing help in using the optimally tuned range-separated hybrid functional ($\omega$B97X-D3) method.
(1) Yang, Z.; Mao, Z.; Xie, Z.; Zhang, Y.; Liu, S.; Zhao, J.; Xu, J.; Chi, Z.; Aldred, M. P. Recent advances in organic thermally activated delayed fluorescence materials. *Chem. Soc. Rev.* 2017, 46, 915–1016.

(2) Yao, Y.; Yuan, K.; Chen, T.; Xu, P.; Li, H.; Chen, R.; Zheng, C.; Zhang, L.; Huang, W. Thermally Activated Delayed Fluorescence Materials Towards the Breakthrough of Organoelectronicos. *Adv. Mater.* 2014, 26, 7931–7958.

(3) Highly Efficient OLEDs Materials Based on Thermally Activated Delayed Fluorescence; Yersin, H., Ed.; Wiley-VCH: Weinheim, Germany, 2019.

(4) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. High efficiency organic light-emitting diodes from delayed fluorescence. *Nature* 2012, 492, 234–238.

(5) Czerwiec, R.; Leitl, M. J.; Homeier, H. H. H.; Yersin, H. Cu(I) complexes – Thermally activated delayed fluorescence. Photophysical approach and material design. *Coord. Chem. Rev.* 2016, 325, 2–28.

(6) Wong, M. Y.; Zysman-Colman, E. Purely organic thermally activated delayed fluorescence for organic light-emitting diodes. *Adv. Mater.* 2017, 29, 1605444.

(7) Liu, Y.; Li, C.; Ren, Z.; Yan, S.; Bryce, M. R. All organic thermally activated delayed fluorescence materials for organic light-emitting diodes. *Nat. Rev. Mater.* 2018, 3, 18020.

(8) Lv, L.; Yuan, K.; Si, C.; Zuo, G.; Wang, Y. Mechanism study of TADF and phosphorescence in dinuclear copper (I) molecular crystal using QM/MM combined with an optimally tuned range-separated hybrid functional. *Org. Electron.* 2020, 81, 105667–105679.

(9) Noda, H.; Nakonatani, H.; Adachi, C. Excited state engineering for efficient intersystem crossing. *Sci. Adv.* 2018, 4, No. eaao6910.

(10) Noda, H.; Chen, X.-K.; Nakonatani, H.; Hosokai, T.; Miyajima, M.; Notsuka, N.; Kashima, Y.; Brédas, J.-L.; Adachi, C. Critical role of intermediate electronic states for spin-flip processes in charge-transfer-type organic molecules with multiple donors and acceptors. *Nat. Mater.* 2019, 18, 1084–1090.

(11) Cui, L.-S.; Gillett, A. J.; Zhang, S.-F.; Ye, H.; Liu, Y.; Chen, X.-K.; Lin, Z.-S.; Evans, E. W.; Myers, W. K.; Ronson, T. K.; Nakonatani, H.; Reineke, S.; Brédas, J.-L.; Adachi, C.; Friend, R. H. Spin-flip enables efficient and stable organic electroluminescence from charge-transfer states. *Nat. Photonics* 2020, 14, 636–642.

(12) Penfold, T. J.; Gindensperger, E.; Daniel, C.; Marian, C. M. Spin-vibronic mechanism for intersystem crossing. *Chem. Rev.* 2018, 118, 6975–7025.

(13) Wang, M.; Chatterjee, T.; Foster, C. J.; Wu, T.; Yi, C.-L.; Yu, H.; Wong, K.-T.; Hu, B. Exploring mechanism of generating spin-orbital coupling through donor-oracceptor design to realize spin flipping in thermally activated delayed fluorescence. *J. Mater. Chem. C* 2020, 8, 3395–3401.

(14) Rausch, A. F.; Homeier, H. H. H.; Yersin, H. Organometallic Pt(II) and Ir(III) triplet emitters for OLED applications and the role of spin–orbit coupling: A study based on high-resolution optical spectroscopy. *Top. Organomet. Chem.* 2010, 29, 193–235.

(15) Yersin, H.; Mataranga-Popa, L.; Czerwiec, R.; Dovbii, Y. Design of a new mechanism beyond thermally activated delayed fluorescence toward fourth generation organic light emitting diodes. *Chem. Mater.* 2019, 31, 6110–6116.

(16) Yersin, H.; Mataranga-Popa, L.; Li, S.-W.; Czerwiec, R. Design strategies for materials showing thermally activated delayed fluorescence and beyond: Towards the fourth-generation OLED mechanism. *J. Soc. Inf. Disp.* 2018, 26, 194–199.

(17) Baryshnikov, G.; Minea, B.; Agren, H. Theory and calculation of the phosphorescence phenomenon. *Chem. Rev.* 2017, 117, 6500–6537.

(18) Shafikov, M. Z.; Suleymanova, A. F.; Czerwiec, R.; Yersin, H. Design strategy for Ag(I)-based thermally activated delayed fluorescence reaching an efficiency breakthrough. *Chem. Mater.* 2017, 29, 1708–1715.

(19) Shafikov, M. Z.; Suleymanova, A. F.; Czerwiec, R.; Yersin, H. Thermally activated delayed fluorescence from Ag(I) complexes: A route to 100% quantum yield at unprecedentedly short decay time. *Inorg. Chem.* 2017, 56, 13274–13285.

(20) de Souza, B.; Farias, G.; Neese, F.; Izsák, R. Predicting phosphorescence rates of light organic molecules using time-dependent density functional theory and the path integral approach to dynamics. *J. Chem. Theory Comput.* 2019, 15, 1896–1904.

(21) Neese, F. Software update: the ORCA program system, version 4.0. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2018, 8, No. e1327.

(22) Becker, A. D. Density-functional exchange-energy approximation with correct asymmetric behavior. *Phys. Rev. A* 1988, 38, 3098–3100.

(23) Vahtras, O.; Almlof, J.; Fyereisen, M. W. Integral approximations for LCAO-SCF calculations. *Chem. Phys. Lett.* 1993, 213, 514–518.

(24) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* 2005, 7, 3297–3305.

(25) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate Ab Initio parametrization of density functional dispersion correction (DFT-D) for the 94 Elements H-Pu. *J. Phys. Chem. 2010, 132, 154104.

(26) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* 2011, 32, 1456–1465.

(27) Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. Energy-adjusted ab initio pseudo potentials for the second and third row transition elements. *Theor. Chem. Acta 1990, 77, 123–141.

(28) Körzdörfer, T.; Brédas, J. L. Organic electronic materials: Recent advances in the DFT description of the ground and excited states using tuned range-separated hybrid functionals. *Acc. Chem. Res. 2014, 47, 3284–3291.

(29) Sun, H.; Zhong, C.; Brédas, J.-L. Reliable prediction with tuned range-separated functionals of the singlet–triplet gap in organic emitters for thermally activated delayed fluorescence. *J. Chem. Theory Comput.* 2015, 11, 3851–3858

(30) Lu, T. optDFTw and scanDFTw program v1.0. http://sobereva.com/346 (2017.3.8).

(31) Sandhöfer, B.; Neese, F. One-electron contributions to the g-tensor for second-order Douglas-Kroll-Hess theory. *J. Phys. Chem. 2012, 137, 094102.

(32) Weigend, F. Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* 2006, 8, 1057–1065.

(33) Neese, F.; Wennmöhs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree–Fock and hybrid DFT calculations. A ‘chain-of-spheres’ algorithm for the Hartree–Fock exchange. *Chem. Phys.* 2009, 356, 98–109.

(34) Barone, V.; Cossi, M. Quantum calculation of molecular energies and energy gradients in solution by a Conductor Solvent Model. *J. Phys. Chem. A* 1998, 102, 1995–2001.

(35) Roemelt, M.; Maganas, D.; DeBeer, S.; Neese, F. A combined DFT and restricted open-shell configuration interaction method including spin-orbit coupling: Application to transition metal L-edge X-ray absorption spectroscopy. *J. Chem. Phys.* 2013, 138, 204101.

(36) Neese, F. Efficient and accurate approximations to the molecular spin-orbit coupling operator and their use in molecular g-tensor calculations. *J. Chem. Phys.* 2005, 122, 034107.

(37) Schatz, G. C.; Ratner, M. A. Quantum Chemistry in Chemistry, 1st ed.; Dover Publications: Mineola, N.Y, 2002.

(38) de Souza, B.; Neese, F.; Izsák, R. On the theoretical prediction of fluorescence rates from first principles using the path integral approach. *J. Chem. Phys.* 2018, 148, 034104.

(39) Daza, M. C.; Doerr, M.; Salzmann, S.; Marian, C. M.; Thiel, W. Photophysics of phenalenone: quantum-mechanical investigation of singlet–triplet intersystem crossing. *Phys. Chem. Chem. Phys.* 2009, 11, 1688–1696.
(40) Baiardi, A.; Bloino, J.; Barone, V. General time dependent approach to vibronic spectroscopy including Franck–Condon, Herzberg–Teller, and Duschinsky Effects. *J. Chem. Theory Comput.* 2013, 9, 4097−4115.

(41) Minaev, B.; Wang, Y.-H.; Wang, C.-K.; Luo, Y.; Ågren, H. Density functional theory study of vibronic structure of the first absorption Q x band in free-base porphin. *Spectrochim. Acta, Part A* 2006, 65, 308−323.

(42) Scholz, R.; Kleine, P.; Lygaitis, R.; Popp, L.; Lenk, S.; Etherington, M. K.; Monkman, A. P.; Reineke, S. Investigation of thermally activated delayed fluorescence from a donor–acceptor compound with time-resolved fluorescence and density functional theory applying an optimally tuned range-separated hybrid functional. *J. Phys. Chem. A* 2020, 124, 1535−1553.

(43) Xu, H.; Wang, M.; Yu, Z.-G.; Wang, K.; Hu, B. Magnetic field effects on excited states, charge transport, and electrical polarization in organic semiconductors in spin and orbital regimes. *Adv. Phys.* 2019, 68, 49−121.

(44) Neese, F. Importance of direct spin−spin coupling and spin-flip excitations for the zero-field splittings of transition metal complexes: A case study. *J. Am. Chem. Soc.* 2006, 128, 10213−10222.

(45) Neese, F. Quantum chemistry and EPR parameters. *eMagRes* 2017, 6, 1−22.

(46) Bora, P. L.; Novotný, J.; Ruud, K.; Komorovsky, S.; Marek, R. Electron-spin structure and metal-ligand bonding in open-shell systems from relativistic EPR and NMR: A case study of square-planar iridium catalysts. *J. Chem. Theory Comput.* 2019, 15, 201−214.