Evidence and mechanism of efficient thermally activated delayed fluorescence promoted by delocalized excited states

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The design of organic compounds with nearly no gap between the first excited singlet (S1) and triplet (T1) states has been demonstrated to result in an efficient spin-flip transition from the T1 to S1 state, that is, reverse intersystem crossing (RISC), and facilitate light emission as thermally activated delayed fluorescence (TADF). However, many TADF molecules have shown that a relatively appreciable energy difference between the S1 and T1 states (~0.2 eV) could also result in a high RISC rate. We revealed from a comprehensive study of optical properties of TADF molecules that the formation of delocalized states is the key to efficient RISC and identified a chemical template for these materials. In addition, simple structural confinement further enhances RISC by suppressing structural relaxation in the triplet states. Our findings aid in designing advanced organic molecules with a high rate of RISC and, thus, achieving the maximum theoretical electroluminescence efficiency in organic light-emitting diodes.

INTRODUCTION
One of the most effective ways to enhance internal electroluminescence (EL) quantum efficiency (ηint) in organic light-emitting diodes (OLEDs) is well recognized to be the management of the pathways between excited singlet (S) and triplet (T) states. In OLEDs, the effective use of triplets is fundamental for achieving high ηint because one singlet is generated for every three triplets based on spin statistics under electrical excitation (Fig. 1A) (1). Although a spin-flip from pure S to pure T states that is, intersystem crossing (ISC), is generally forbidden because of their different spin multiplicities, it becomes possible when their wave functions are mixed through spin-orbital coupling (SOC). The degree of mixing (λ) can be simply expressed as λ = HSO/ΔE_ST, where HSO and ΔE_ST are the SOC constant and energy difference between the S1 and T1 states, respectively (2). By incorporating a heavy atom such as iridium into organic molecules, HSO is enhanced and a strong mixing of the spin orbitals of the S and T states is induced, resulting in efficient radiative decay from T1 to the ground state (S0), that is, phosphorescence, with nearly 100% of photoluminescence (PL) quantum yield (PLQY) (3).

Alternatively, the λ can be enhanced by decreasing ΔE_ST, which can also open a pathway from lower-energy T1 to higher-energy S1, that is, reverse ISC (RISC), when ΔE_ST is small enough. On the basis of quantum chemical theory, ΔE_ST is proportional to the exchange energy, which is related to the overlap integral between the two open-shell orbitals responsible for the isoconfigurational S and T states, and is typically ~1 eV for conventional condensed polyacrylate aromatic compounds, such as anthracene (4). Because the HSO of aromatic compounds is also small, RISC is generally negligible. However, when the ΔE_ST of aromatic compounds is also small, RISC is generally negligible. However, when the ΔE_ST approaches the thermal energy (~26 meV at room temperature), RISC is induced via thermal excitation, and delayed fluorescence (DF) is subsequently emitted from S1. This is so-called thermally activated DF (TADF), and recent extensive studies on TADF-OLEDs have revealed ηint values of nearly 100% (5–11). According to the semiclassical model of TADF, the rate constant for RISC (kRISC) is given by kRISC = A × exp(−ΔE_ST/kBT), where A is the pre-exponential factor including HSO, k_B is the Boltzmann constant, and T is the temperature (12). Therefore, a high kRISC can be achieved by decreasing ΔE_ST. However, although this idea has been supported by many experimental results, as shown in Fig. 1B (5, 13–19), several papers report fairly high kRISC values even for large ΔE_ST of a few hundred millielectron volts (6, 20). For instance, carbazole-benzonitrile (CzBN) derivatives synthesized by Zhang et al. (20, 21) were reported to have a ΔE_ST of ~0.2 eV. Although the ΔE_ST is too large for efficient RISC at room temperature, CzBN-based OLEDs showed high external EL quantum efficiencies (ηEQE) of ~20%. This ηEQE value means that, under an assumption of a light outcoupling efficiency of OLEDs (22), all the excitons generated electrically were used for EL.

A number of fundamental studies using transient PL (TR-PL) spectroscopy and theoretical calculations have been devoted to understand the mechanism of efficient RISC upon a large ΔE_ST of several hundred millielectron volts (6, 23–27). In particular, Dias et al. (25) and Gibson et al. (27) have proposed that the second-order SOC involving the locally excited T state (4LE) and charge-transfer (CT) excited T state (4CT) in thermal equilibrium is crucial for efficient RISC. In the scenario, the spin-allowed transition of 4LE to CT excited S state (4CT) in materials having a large ΔE_ST is facilitated efficiently by the vibronic coupling between the 4LE and 4CT states (25, 27). This suggests that RISC is a dynamical process in an excited state. However, this study has been thoroughly conducted for only a few molecules, which consist of a near-orthogonal electron donor (D) and acceptor (A) units. Still, a deeper understanding of the mechanism leading to
efficient RISC based on a direct observation of excited states formed in both the S and T states is needed to clarify the relationship to the chemical structure and will provide a strategy for the advanced molecular design of TADF molecules.

Here, we used a comprehensive set of complementary experimental techniques, with an emphasis on transient absorption spectroscopy (TAS), to demonstrate that $k_{\text{RISC}}$ cannot be determined by the $D_{\text{ST}}$ alone and strongly relies on the excited states. To understand the mechanism, we focused on Cz-phthalonitrile (CzPN) (5) and CzBN (20, 21) derivatives: 4CzIPN, 2CzBN, o-3CzBN, m-3CzBN, p-3CzBN, 4CzBN, and 5CzBN (Fig. 1C). Unlike the CzPN derivatives reported previously by our group (5, 19), CzBN derivatives have similar $\Delta E_{\text{ST}}$ values (~0.2 ± 0.04 eV) (see Table 1). In this sense, similar $k_{\text{RISC}}$ values might be expected for CzBN derivatives, but the result is completely different. By looking at excited-state dynamics using TAS, we are able to attribute the different $k_{\text{RISC}}$ to the formation of delocalized excited states, which facilitates RISC. We also identify that a linearly positioned Cz pair in a D-A-D structure (Fig. 1D) is the structural requirement for the formation of delocalized excited state. Our findings provide an advanced general design for TADF molecules with high $k_{\text{RISC}}$ and facilitate the deeper understanding of significant spin up-conversion processes (2).

**RESULTS**

Before examining the excited-state dynamics, we evaluated the fundamental photophysical properties of the CzBN derivatives (Table 1). TR-PL profiles of the CzBN derivatives in oxygen-free toluene show strong DF for 4CzBN and 5CzBN and weak DF for p-3CzBN, but no DF for 2CzBN, o-3CzBN, or m-3CzBN (Fig. 2A). The observed DF
completely vanished in the presence of oxygen, indicating that the DF is emitted via T states. In Table 1, the $k_{\text{RISC}}$ values of 4CzBN (1.8 $\times$ 10$^5$ s$^{-1}$) and 5CzBN (2.4 $\times$ 10$^5$ s$^{-1}$) are larger than the $k_{\text{RISC}}$ value of 3Cz2BN (0.12 $\times$ 10$^5$ s$^{-1}$) by one order of magnitude despite similar $\Delta E_{\text{ST}}$ values of $\sim$0.20 eV for the three materials (Fig. 2B). Moreover, although the $\Delta E_{\text{ST}}$ of 3Cz2BN is almost the same as that of 4CzBN, 3Cz2BN showed no appreciable DF, that is, $k_{\text{RISC}} \sim$ 0 s$^{-1}$. The rate constants for nonradiative decay of the triplet states ($k_{\text{nr}}$), a competing parameter of $k_{\text{RISC}}$, are of the same order of magnitude for the three 3CzBN isomers, $k_{\text{nr}} \sim$ 10$^7$ s$^{-1}$, although their $k_{\text{RISC}}$ values differ by four orders of magnitude (Table 1). This result indicates that the TADF is activated by the large $k_{\text{RISC}}$ and not because of the suppression of the nonradiative decay path of the triplet states.

When doped at a concentration of 15 weight % (wt %) in a 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT) matrix, 5CzBN showed a PLQY of 78 $\pm$ 2%, and OLEDs using 5CzBN reached an $\eta_{\text{BEQE}}$ of $\sim$24% (Fig. 2C), indicating that 5CzBN can intrinsically harvest almost all excitons for light emission in the OLEDs with the help of RISC. Here, we note that the 15 wt % 4CzBN–doped PPT films show a PLQY comparable with that of 5CzBN. However, the $\eta_{\text{BEQE}}$ of the 4CzBN-based OLEDs showed a slightly lower value of $\sim$20%, presumably because of a lower charge carrier balance in the devices. Although 15 wt % p-3CzBN–doped PPT films show a low PLQY of 31 $\pm$ 2%, the $\eta_{\text{BEQE}}$ of p-3CzBN–based OLEDs (4.5%) is much higher than the theoretical limit of $\eta_{\text{BEQE}}$ for ordinary fluorescent OLEDs considering a similar PLQY (1.6 to 2.3%), where a light outcoupling efficiency of 20 to 30% and an exciton generation ratio of singlets of 25% are assumed (22), indicating that TADF from p-3CzBN contributes to $\eta_{\text{BEQE}}$. These photophysical properties and OLED characteristics imply that $k_{\text{RISC}}$ cannot be predicted by $\Delta E_{\text{ST}}$ only, and instead, the bonding configuration of D to A moieties plays an essential role for the CzBN derivatives to increase $k_{\text{RISC}}$ and enhance $\eta_{\text{BEQE}}$.

To understand the large difference in $k_{\text{RISC}}$ by the structural modifications, we investigated the excited-state dynamics of CzPN and CzBN derivatives using TAS (28–30). We measured the absorption change ($\Delta OD$; OD, optical density) caused by the presence of photoexcited states of not only S$_1$ and T$_1$ but also intermediate excited states as a function of delay time ($\Delta t$). Figure 3A shows the TAS spectra of 4CzIPN ($\Delta t = 3$ ps and 4.6 $\mu$s) and 2CzBN ($\Delta t = 3$ ps and 30 $\mu$s) in toluene. The TAS profiles over the full measured range of $\Delta t$ are illustrated in Fig. 3B as contour maps. The contour maps of both molecules show that the TAS spectra change in the vicinity of ISC, as judged from the time constant of the prompt fluorescence ($\tau_{\text{prompt}}$) determined by TR-PL (Fig. 3C). We found that the spectral shape for $\Delta t > \tau_{\text{prompt}}$ stays unchanged for each molecule because of the almost identical decay lifetimes of T features (fig. S1) (the assignment is described below). In addition, we confirmed that the lifetime of the T features for 4CzIPN are nearly the same as the $\tau_{\text{DF}}$ determined by TR-PL (fig. S1). These results indicate that the observed T states are mutually coupled in thermal equilibrium, and facilitate the RISC as a unit for the dynamics of RISC. Therefore, in the following experiments, we focused on the assignment of the excited states of the S and T states (Fig. 3A).

In the time range of $\Delta t = 3$ ps, an intense feature at 860 nm with a small shoulder (760 nm), which greatly resembles features commonly observed for cationic mono-Cz (Cz$^+$) compounds (31, 32), was observed for both molecules. Considering that the absorption spectra of 4CzIPN and 2CzBN showed CT characters (5), we assigned the characteristic features at $\Delta t = 3$ ps to the absorption of Cz$^+$ moieties (Cz$^+$) formed in the S$_1$ state by the photoinduced intramolecular CT transitions (figs. S2 and S3). At the same $\Delta t$, we found another band in the near-infrared region of 4CzIPN. This band is a so-called charge resonance (CR) band (31) or an intercalation CT band (32), and it indicates the formation of a delocalized CT (s-CT) state attributed to an intramolecular dimeric radical Cz (Cz$_2$$^-$) formed by an electronic coupling between a mono-Cz$^+$ and a neutral Cz moiety (Fig. 3D). Specifically, a s-CT state means that the cation charge of Cz$^+$ is delocalized in the Cz$_2$$^-$, whereas the counter anion charge is localized at the acceptor moiety, that is, IPN$^-$ for 4CzIPN. The CR band is seen not only in the S$_1$ state as Cz$_2$$^-$ but also in the T$_1$ state ($\Delta t = 4.6 \mu$s) as Cz$_2$$^-$, together

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<th>$\Phi_{\text{PL, Degassed}}$ (%)</th>
<th>$\Phi_{\text{PL, Solid film}}$ (%)</th>
<th>$\tau_{\text{prompt}}$ (ns)</th>
<th>$\tau_{\text{DF}}$ (µs)</th>
<th>$k_{\text{isc}}^{\text{RISC}}$ (×10$^4$ s$^{-1}$)</th>
<th>$k_{\text{isc}}^{\text{SP}}$ (×10$^4$ s$^{-1}$)</th>
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*PLQY at a concentration of 10$^{-3}$ M in toluene. †PLQY for PPT host matrix doped with 3 wt % (left) or 15 wt % (right) of the emitter. ‡Solution samples. §Rate constant of radiative decay of singlets ($k_{\text{isc}}$), $k_{\text{isc}}$, and $k_{\text{ISC}}$ of the solution samples determined by the method described by Masui et al. (18). ||Energy gap calculated from S$_1$ and T$_1$ energy levels estimated from the threshold of fluorescence spectra and peak (2CzBN) or threshold (others) of phosphorescence spectra (Fig. 2B), respectively. The error is ±0.03 eV. The data of fluorescence and phosphorescence spectra of 2CzPN and 4CzIPN are depicted in fig. S7. ¶Virtual values as determined by measuring a time profile of decay curve of triplet state absorption bands in microsecond-TAS (see figs. S1 and S8). **Value of 4CzIPN-mCP (1.3-bis(N-carbazolyl)benzene) (6 wt %) by Masui et al. (18) and of 4CzIPN-CBP (4,4′-N,N’-dicarbazole-biphenyl) (6 wt %) by Uoyama et al. (5).
with other rising features at 680 and 1070 nm. These rising features were also observed for 2CzPN in the time range of \( \Delta t = 30 \mu s \), but the CR band was not detected. These results indicate that, in the S1 and T1 states, 2CzPN forms a localized CT (loCT) state, whereas 4CzIPN forms both deCT and loCT states in thermal equilibrium. The formation of this delocalized excited T state is consistent with the excited-state scheme for 4CzIPN obtained by time-resolved electron paramagnetic resonance conducted at 77 K (33).

Figure 4A shows contour maps for the TAS results of all six CzBN derivatives in toluene. The TAS spectra at \( \Delta t \) in the vicinity of the prompt of all the derivatives are depicted in fig. S4. In Fig. 4A, 2CzBN shows an absorption band at around 815 nm, which is assigned to \( 1\text{Cz}^+ \) and thus \( \text{lo,1CT} \). After transition through ISC, we found only one T absorption band at around 600 nm. Because the phosphorescence spectrum of 2CzBN (Fig. 2B), with clear vibronic progressions and a long triplet lifetime of \(-5 \) s, was in good agreement with that of tricarbazoyl benzene (TCzB; inset in Fig. 2B), the T1 state of 2CzBN is considered to be the same as that of TCzB and, thereby, is assigned to a localized state on a mono-Cz moiety with pure \( \pi-\pi^* \) character (34). In this context, the T1 absorption band at around 600 nm can be ascribed to the \( \pi-\pi^* \) transition of a neutral mono-Cz state (3LE).

Similar to 2CzBN, the TAS spectra of \( \text{o-3CzBN} \) show a \( 1\text{Cz}^+ \) band at around 850 nm before ISC and a \( 3\text{LE} \) band at around 600 nm after ISC. In addition, \( \text{o-3CzBN} \) exhibited another T band at around 1150 nm. Because the T1 character of \( \text{o-3CzBN} \) is understood as a mixing of the CT and LE states based on the vibronic-less phosphorescence spectrum (Fig. 2B) with a short lifetime (~1 s) (34), the feature at around 1150 nm can be attributed to the absorption of the \( \text{loCT} \) state of \( 3\text{Cz}^+ \) (lo,3CT). These spectral characteristics are also observed for \( \text{m-3CzBN} \), implying the formation of the same excited states.

Finally, we look at the dynamics of TADF-active CzBN derivatives. Clear \( \text{Cz}^+ \) and \( \text{Cz}^2+ \) bands were observed in addition to \( 1\text{Cz}^+, 3\text{LE} \), and \( 3\text{Cz}^+ \) bands for 5CzBN, similar to 4CzIPN, indicating the formation of \( \text{lo,1CT} \) and \( \text{de,1CT} \) in the S1 state and \( 3\text{LE}, \text{lo,3CT} \), and \( \text{de,3CT} \) in...
Fig. 3. Excited-state dynamics of CzPN derivatives. (A) Selected TAS spectra of 4CzIPN (Δt = 3 ps and 4.6 μs) and 2CzPN (Δt = 3 ps and 30 μs). div. division. (B) Contour maps of TAS results of 4CzIPN and 2CzPN obtained by different TAS techniques: microsecond-TAS (top) and nanosecond-TAS (bottom) (29, 30). For (B), ΔOD (color intensity) in each figure is normalized arbitrarily for better visualization. (C) Time profile of TR-PL and ΔOD in TAS results at 860 nm (1Cz+) and 1070 nm (3Cz+) of 2CzPN. The TR-PL shown to overlap with the profile of T feature (1Cz+) illustrates the coincidence of their t. (D) Schematic explanation of the CR band formed by Cz2+ in terms of energy-level diagram.

The formation of the deCT state is also reflected in the electronic structure of the CzBN derivatives. In the ground-state absorption spectra (Fig. 4C) of p-3CzBN, 4CzBN, and 5CzBN, a characteristic CT band is observed as the lowest energy transition (CT1), which differs from the commonly observed CT band (CT1) and π-π* band of Cz moieties. Furthermore, CT1 forms for all the CzBN derivatives, except p-3CzBN and 4CzBN. From these results, we can assign CT1 and CT2 to originate from the formation of loCT and deCT characters, respectively. This assignment is consistent with the TAS results, which suggest that p-3CzBN, 4CzBN, and 5CzBN form a deCT state in the S1 state, whereas other CzBN derivatives exhibit a loCT state. The same consideration is applicable to 4CzIPN and 2CzPN (Fig. 3B and fig. S2).
TADF-active molecules as a pair of Cz units connected linearly with a bridging A unit, that is, at 2- and 5-positions or 3- and 6-positions (Fig. 1D). This structural scheme is regarded as a linear D-A-D structure, and the linearly positioned Cz pair in the D-A-D structure is identified as the origin of the deCT states. Notably, a D-A-D structure has been a common chemical template of TADF molecules, but the linear D-A-D structure proposed here is a new connection rule for the D and A moieties within a category of D-A-D structures. Furthermore, the linear D-A-D structure is extremely simple, and a combination of other kinds of D and A units may facilitate RISC by forming deCT states.

We next discuss a mechanism leading to high $k_{\text{RISC}}$ via deCT in terms of excited-state dynamics. Generally, RISC is intrinsically forbidden between $3\text{CT}$ and $1\text{CT}$ states because of a vanishing of the SOC matrix elements between their molecular orbitals and it is facilitated by SOC between $3\text{LE}$ and $1\text{CT}$ (25, 27). In addition, as Gibson et al. (27) demonstrated theoretically, a vibronic coupling between the $3\text{CT}$ and $3\text{LE}$ states plays a crucial role in the production of $1\text{CT}$ states via RISC. In this context, the energy gap to overcome for RISC is not $\Delta E_{\text{ST}}$ but the energy difference between $3\text{LE}$ and $1\text{CT}$, as here defined to $\Delta E_{\text{ST(LE)}}$, and a mutual coupling among the T states in thermal equilibrium is the key for efficient RISC.
Figure 4D shows $\Delta E_{\text{ST(LE)}}$ and $\Delta E_{\text{ST}}$ of all the CzBN derivatives, which are taken from Fig. 2B. Here, the $^3$LE level observed only for 2CzBN is used as a common one for all the CzBN derivatives because the $^3$LE, which originates from a phenyl-Cz, is not significantly affected by adding acceptor substituents (see the phosphorescence spectrum of 2CzBN and TCzB in Fig. 2B). It is seen that, although the $\Delta E_{\text{ST(LE)}}$ values of the TADF-inactive molecules are similar to their $\Delta E_{\text{ST}}$ values (~0.2 eV), the $\Delta E_{\text{ST(LE)}}$ values of the TADF-active molecules are 0.12, 0.01, and ~0.06 eV for p-3CzBN, 4CzBN, and 5CzBN, respectively, which are all smaller than their corresponding $\Delta E_{\text{ST}}$ values. This result is caused by the lowering of the S1 state for the TADF-active molecules, in line with the formation of a CT2 band in Fig. 4C. In addition, a dependence on $\Delta E_{\text{ST(LE)}}$ appears among the TADF-active molecules. Both 4CzBN and 5CzBN, which exhibit $k_{\text{RISC}}$ values that are one order of magnitude higher than the $k_{\text{RISC}}$ value of p-3CzBN, show smaller $\Delta E_{\text{ST(LE)}}$ values. These data suggest that, for the facilitation of RISC, a $\Delta E_{\text{ST}}$ of ~0.2 eV does not play a role, and instead, a $\Delta E_{\text{ST(LE)}}$ of less than 0.2 eV is needed; a large $k_{\text{RISC}}$ can be achieved by decreasing $\Delta E_{\text{ST(LE)}}$. To verify this idea, a comparison of an activation energy for the RISC among the TADF-active molecules may be needed, but a quite small TADF efficiency of 5CzBN, ~4% at room temperature, made the comparison in the present stage difficult.

Finally, we propose a comprehensive design strategy for TADF molecules to obtain a high PLQY. Although 4CzBN and 5CzBN exhibited comparable $k_{\text{RISC}}$ values, the PLQY of 4CzBN (62%) was lower than that of 5CzBN (85%) in solution (Table 1). This is ascribed to the high $k_{\text{RISC}}$ of 4CzBN, and p-3CzBN was found to have an even higher $k_{\text{RISC}}$. We attribute the high $k_{\text{RISC}}$ to structural relaxation because the PLQY of 4CzBN increases to nearly 100% in a rigid matrix owing to the suppression of $k_{\text{RISC}}$ (1.7 $\times$ 10$^{-4}$ s$^{-1}$ in solution to 3.4 $\times$ 10$^{-4}$ s$^{-1}$ in rigid matrix). For the CzBN derivatives, the most probable relaxation is the twisting of the Cz moieties against the BN core (35). The $k_{\text{RISC}}$ of p-3CzBN was a few times higher than that of 5CzBN because there is no Cz at the 5-position, and twisting of the Cz moiety at the 6-position can easily occur (Fig. 1C). The absence of Cz at the 4-position for 4CzBN still produces the twisting of Cz moiety at 3- and 5-positions. As a result, the twisting of all the Cz moieties becomes most difficult for 5CzBN owing to the strong steric hindrance around each Cz moiety.

According to the Mulliken-Hush theory, the peak top of a CR band ($V_{\text{CR}}$) is proportional to the electronic coupling (V) between the two redox sites (35); thus, the degree of structural relaxation can be rationalized by the $V_{\text{CR}}$ in the linearly positioned Cz pair. The $V_{\text{CR}}$ gradually shifts to lower energies in the order of p-3CzBN > 4CzBN > 5CzBN (Fig. S6), indicating that p-3CzBN forms a more planar D-A-D structure in the T1 state because of V and, thus, $V_{\text{CR}}$ increases when the twisting angle of the D moieties becomes smaller (32). Therefore, we conclude that binding the linearly positioned Cz pair with surrounding bulky groups suppresses the structural relaxation, thereby contributing to a decreased $k_{\text{RISC}}$, while keeping a high $k_{\text{RISC}}$. Consequently, the most rigid molecule, 5CzBN, shows the highest PLQY owing to the largest $k_{\text{RISC}}$ and lowest $k_{\text{RISC}}$.

In summary, we clarified that the formation of a $^{4}\text{CT}$ is a driving force to promote a large $k_{\text{RISC}}$ even when $\Delta E_{\text{ST}}$ is not close to zero. We also pointed out the importance of the suppression of the structural relaxation in the T1 state to achieve a high PLQY. For CzBN derivatives, twisting of the linearly positioned Cz pair connected to the A-unit plane may occur depending on the free space around the Cz pair. This causes the structural relaxation to deactivate the T1 state. Accordingly, we propose a chemical structure to form $^{4}\text{CT}$ while suppressing the structural relaxation by introducing bulky moieties around linearly positioned D units in a D-A-D structure. The simple design strategy established here will be extremely beneficial for the design of new TADF molecules, and we believe that our work contributes to the progression of photochemistry and the development of high-performance OLEDs, as well as future molecular light-emitting devices.

**MATERIALS AND METHODS**

**Materials**

4CzIPN, 2CzIPN, m-3CzBN, 4CzBN, and 5CzBN were synthesized according to literature procedures (5, 20, 21). 2CzBN, o-3CzBN, and p-3CzBN were newly synthesized. The synthetic procedures and characterization are described in the Supplementary Materials. All the materials were purified by thermal sublimation. Solutions were prepared by dissolving the purified molecules in toluene (purity, 99.8%). The solution concentration was 10$^{-3}$ to 10$^{-5}$ M, depending on the samples and measurements.

**Optical characterization of TADF molecules**

The solutions were characterized by measuring the steady-state ultraviolet-visible (UV-VIS) absorption/PL spectra and TR-PL. TR-PL was measured using a C11367-01 spectrometer (Hamamatsu Photonics) or a Fluorocube fluorescence lifetime system (HORIBA). The PLQY of the solutions was measured by an absolute PLQY measurement system (C11347-01, Hamamatsu Photonics), with an excitation wavelength of 337 nm. Before the TAS and TR-PL measurements, the solutions were deoxygenated with dry nitrogen gas to eliminate the deactivation of triplets. The effect of deoxygenation was confirmed by comparing $\tau_{\text{prompt}}$ and $\tau_{\text{TADF}}$ values with those reported by Uoyama et al. (5).

**OLED fabrication and characterization**

Glass substrates with a prepatterned, 100-nm-thick, 100 ohm/square tin-doped indium oxide (ITO) coating were used as anodes. After pre-cleaning of the substrates, effective device areas of 4 mm$^2$ were defined on the patterned ITO substrates by a polyimide insulation layer using a conventional photolithography technique. Organic layers were formed by thermal evaporation. Doped emitting layers were deposited by coevaporation. Deposition was performed under vacuum at pressures <5 $\times$ 10$^{-3}$ Pa. After device fabrication, devices were immediately encapsulated with glass lids using epoxy glue in a nitrogen-filled glove box [$O_2 < 0.1$ parts per million (ppm) and $H_2O < 0.1$ ppm]. OLEDs with the structure ITO/4’-cyclohexylidenediis[N,N-bis(4-methylphenyl)benzeneamine] (TAPC) (35 nm)/mCP (10 nm)/dopant (15 wt%):PPT (30 nm)/PPT (40 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated. The current density–voltage–luminance characteristics of the OLEDs were evaluated using a source measurement meter (B2912A, Agilent) and a calibrated spectroradiometer (CS-2000A, Konica Minolta Sensing Inc.). EL spectra were collected using a spectroradiometer (simultaneously with luminance). The $\eta_{\text{EQE}}$ was calculated from the front luminance, current density, and EL spectrum. All measurements were performed under an ambient atmosphere at room temperature.
TAS measurements

Femtosecond-, nanosecond-, and microsecond-TAS measurements were conducted using different apparatuses developed in-house (28–30). For femtosecond-TAS, the output from a Ti:Al2O3 regenerative amplifier [Spectra-Physics, Hurricane, 800 nm; full width at half maximum (FWHM) pulse, 130 fs; repetition, 1 kHz] was used as the laser source. The wavelength of the pump laser was 400 nm, which is a second harmonic of the fundamental light (800 nm) generated by a β-barium borate crystal, whereas the white-light continuum generated by focusing the fundamental beam (800 nm) onto a sapphire plate (2 mm thick) was used as the probe light. For nanosecond-TAS, we used the third harmonic of fundamental light (1064 nm) of a Nd3+:YAG laser (wavelength, 355 nm; FWHM pulse, <150 ps; repetition, 10 Hz) as the pump light and a xenon flash lamp as the probe light. The system of nanosecond-TAS was used for microsecond-TAS measurements, but the probe light was exchanged with a xenon steady-state lamp. Although the strong intensity of the flash lamp was suitable for measurements with a fast response time (~1 ns), the use of the steady lamp could cover Δt ~ 100 ns with a slow response time of 10 to 30 ns. The irradiated intensity of the pump laser was set to 0.21 and 0.27 mJ/cm² for femtosecond-TAS measurements of 4CzIPN and 2CzPN, respectively, and 0.7 to 1.4 mJ/cm² for nanosecond- and microsecond-TAS of all the derivatives. After the TAS measurements, UV–VIS absorption spectra were measured to check the sample degradation by laser irradiation. We noted that the long-duration irradiation of the femtosecond-pulse laser gave rise to a decrease of a first CT band in the UV–VIS absorption spectra, in particular for 4CzIPN (fig. S2). Therefore, we carefully conducted the TAS measurements by checking the data reproducibility. All measurements were carried out at 295 K. In Fig. 3A, ΔOD of the microsecond-TAS spectra at Δt = 4.6 and 30 μs was corrected with reference to the intensity of nanosecond-TAS at Δt = 27 ns; the ΔOD of the nanosecond-TAS was also corrected in advance using femtosecond-TAS at Δt = 2 ns. The linearity of ΔOD for each correcting process was guaranteed by considering the time resolution of microsecond- and nanosecond-TAS measurements.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/5/e1603282/DC1

Synthesis and characterization of 2CzBN, α-3CzBN, and p-3CzBN

Table S1. Time profiles of TAS of various triplet states of 4CzIPN and 2CzPN in toluene.

Table S2. Steady-state absorption spectra.

Table S3. Laser power dependence in TAS spectra.

Table S4. TAS results of 3, 4, 6-p-CzBN.

Table S5. Energy position of CR band.

Table S7. Emission spectra of CR bands.

Table S8. Emission spectra of CR bands.


REFERENCES AND NOTES


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Evidence and mechanism of efficient thermally activated delayed fluorescence promoted by delocalized excited states
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