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

Takuya Hosokai,1,2* Hiroyuki Matsuzaki,1,2 Hajime Nakanotani,3,4* Katsumi Tokumaru,2 Tetsuo Tsutsui,2 Akihiro Furube,1,2† Keirou Nasu,5 Hiroko Nomura,5 Masayuki Yahiro,6 Chihaya Adachi3,4

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 ($\eta_{\text{int}}$) 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 $\eta_{\text{int}}$ 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 ($\lambda$) can be simply expressed as $\lambda = H_{\text{SO}}/\Delta E_{\text{ST}}$, where $H_{\text{SO}}$ and $\Delta E_{\text{ST}}$ 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, $H_{\text{SO}}$ is enhanced and the 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 $\lambda$ can be enhanced by decreasing $\Delta E_{\text{ST}}$, which can also open a pathway from lower-energy T1 to higher-energy S1, that is, reverse ISC (RISC), when $\Delta E_{\text{ST}}$ is small enough. On the basis of quantum chemical theory, $\Delta E_{\text{ST}}$ 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 polycyclic aromatic compounds, such as anthracene (4). Because the $H_{\text{SO}}$ of aromatic compounds is also small, RISC is generally negligible. However, when the $\Delta E_{\text{ST}}$ 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 $\eta_{\text{int}}$ values of nearly 100% (5–11). According to the semiclassical model of TADF, the rate constant for RISC ($k_{\text{RISC}}$) is given by $k_{\text{RISC}} \sim A \times \exp(-\Delta E_{\text{ST}}/k_{\text{B}}T)$, where A is the pre-exponential factor including $H_{\text{SO}}$, $k_{\text{B}}$ is the Boltzmann constant, and T is the temperature (12). Therefore, a high $k_{\text{RISC}}$ can be achieved by decreasing $\Delta E_{\text{ST}}$. However, although this idea has been supported by many experimental results, as shown in Fig. 1B (5, 13–19), several papers report fairly high $k_{\text{RISC}}$ values even for large $\Delta E_{\text{ST}}$ of a few hundred millielectron volts (6, 20). For instance, carbazol-benzonitrile (CzBN) derivatives synthesized by Zhang et al. (20, 21) were reported to have a $\Delta E_{\text{ST}}$ of ~0.2 eV. Although the $\Delta E_{\text{ST}}$ is too large for efficient RISC at room temperature, CzBN-based OLEDs showed high external EL quantum efficiencies ($\eta_{\text{EQE}}$) of ~20%. This $\eta_{\text{EQE}}$ 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 $\Delta E_{\text{ST}}$ 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 (LE) and charge-transfer (CT) excited T state (CT) in thermal equilibrium is crucial for efficient RISC. In the scenario, the spin-allowed transition of LE to CT excited S state (CT) in materials having a large $\Delta E_{\text{ST}}$ is facilitated efficiently by the vibronic coupling between the LE and CT 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 $\Delta E_{\text{ST}}$ 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, 2CzPN, 2CzBN, $\sigma$-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 ($\sim$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, $\sigma$-3CzBN, or $m$-3CzBN (Fig. 2A). The observed DF

---

**Fig. 1. EL mechanism.** (A) Schematic of electrical exciton generation and EL mechanism in TADF-OLEDs. (B) Relationship between experimentally determined $k_{\text{RISC}}$ and $\Delta E_{\text{ST}}$ in previous works (5, 13–19) and this work. The $k_{\text{RISC}}$ values of (4) to (6), treating to $\sim$0 s$^{-1}$, are below the limit of the estimation because of nearly no or undetectably weak DF intensity (Fig. 2A, inset). (C) Molecular structures of CzPN and CzBN derivatives, highlighting linearly positioned Cz moieties (blue). The numbering of the substituent positions of the BN core is depicted for 2CzBN. (D) D and A units of the CzPN and CzBN derivatives and D-A-D structure constructed with a linearly positioned Cz pair. R indicates substituents with electron-accepting properties, such as cyano groups.
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 \( \eta_{\text{RISC}} \) of 3CzBN (0.12 \( \times 10^5 \) s\(^{-1} \)) by one order of magnitude despite similar \( \Delta E_{\text{ST}} \) values of \( \pm 0.20 \) eV for the three materials (Fig. 2B). Moreover, although the \( \eta_{\text{RISC}} \) of 3CzBN is almost the same as that of 4CzBN, 3CzBN showed no appreciable DF, that is, \( k_{\text{RISC}} \sim 0 \) s\(^{-1} \). The rate constants for nonradiative decay of the triplet states \( (k_{\text{nr}}^T) \), a competing parameter of \( k_{\text{RISC}} \), are of the same order of magnitude for the three 3CzBN isomers, \( k_{\text{nr}}^T \sim 10^4 \) 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 \( \eta_{\text{QE}} \) 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 \( \eta_{\text{QE}} \) 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 % \( \rho \)-3CzBN–doped PPT films show a low PLQY of 31 \pm 2\%, the \( \eta_{\text{QE}} \) of \( \rho \)-3CzBN–based OLEDs (\( \sim 4.5\% \)) is much higher than the theoretical limit of \( \eta_{\text{QE}} \) 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 assured (22), indicating that TADF from \( \rho \)-3CzBN contributes to \( \eta_{\text{QE}} \). 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 \( \eta_{\text{QE}} \).

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 changes (\( \Delta \text{OD} \); 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 2CzPN (\( \Delta t = 3 \) 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 lifetimes 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 2CzPN showed CT characters (5), we assigned the characteristic features at \( \Delta t = 3 \) ps to the absorption of Cz\(^{+} \) moieties (Cz\(^{3+} \)) 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 interwell CT band (32), and it indicates the formation of a delocalized CT (\( ^{\infty} \text{CT} \)) state attributed to an intramolecular dimeric radical Cz (Cz\(^{3+} \)) formed by an electronic coupling between a mono-Cz\(^{+} \) and a neutral Cz moiety (Fig. 3D). Specifically, a \( ^{4} \text{CT} \) state means that the cation charge of Cz\(^{+} \) is delocalized in the Cz\(^{3+} \), 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 \( ^{3} \text{Cz}^{3+} \) but also in the \( T_1 \) state (\( \Delta t = 4.6 \) ms) as \( ^{3} \text{Cz}^{3+} \), together
with other rising features at 680 and 1070 nm. These rising features were also observed for 2CzPN in the time range of $\Delta t = 30$ μs, 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 $\Delta t$ 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 $1Cz^+$ and thus $lo,1CT$. 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 tricarbazolyl 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 π-π* character (34). In this context, the T1 absorption band at around 600 nm can be ascribed to the $p-p^*$ transition of a neutral mono-Cz state (3LE).

Similar to 2CzBN, the TAS spectra of $o$-3CzBN show a $1Cz^+$ band at around 850 nm before ISC and a 3LE band at around 600 nm after ISC. In addition, $o$-3CzBN exhibited another T band at around 1150 nm. Because the T1 character of $o$-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 loCT state of 3Cz+ (lo,3CT). These spectral characteristics are also observed for $m$-3CzBN, implying the formation of the same excited states.

Finally, we look at the dynamics of TADF-active CzBN derivatives. Clear $Cz^+$ and $Cz^2$ bands were observed in addition to $1Cz^+$, 3LE, and $Cz^2$ bands for 5CzBN, similar to 4CzIPN, indicating the formation of $lo,CT$ and $de,1CT$ in the S1 state and $3LE$, $lo,CT$, and $de,CT$ in...
the T_1 state, respectively. On the other hand, for 4CzBN, \(^1\text{Cz}^+\) and \(^1\text{Cz}_2^+\) bands were observed in the S_1 state, but no \(^3\text{Cz}^+\) band was seen after relaxation via ISC and only \(^3\text{Cz}^+\) and strong \(^3\text{Cz}_2^+\) bands were formed (see also Fig. 4B). The phosphorescence spectra of 4CzBN and p-3CzBN show rather vibronic-less features resembling their fluorescence spectra (see Fig. 2B), indicating a strong CT character in the T_1 state (34) because of the formation of de\(^{3}\)CT state. For p-3CzBN, the TAS spectra were essentially the same as those of 4CzBN, except for the energy positions, suggesting a similar T_1 character and RISC process as for 4CzBN.

The formation of the de\(^{3}\)CT 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 (CT2), which differs from the commonly observed CT band (CT1) and \(\pi-\pi^*\) 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 lo\(^{3}\)CT and de\(^{3}\)CT characters, respectively. This assignment is consistent with the TAS results, which suggest that p-3CzBN, 4CzBN, and 5CzBN form a de\(^{3}\)CT state in the S_1 state, whereas other CzBN derivatives exhibit a lo\(^{3}\)CT state. The same consideration is applicable to 4CzIPN and 2CzPN (Fig. 3B and fig. S2).

**DISCUSSION**

The combined results of all structural, photophysical, excited-state, and OLED studies provide a comprehensive answer to the question of why \(k_{\text{RISC}}\) of the CzBN derivatives does not necessarily depend on \(\Delta E_{\text{ST}}\). Molecules exhibiting TADF showed de\(^{3}\)CT states (that is, \(^1\text{Cz}_2^+\) and \(^3\text{Cz}_2^+\)) and a \(^3\text{LE}\) state, whereas TADF-inactive molecules exhibited only a \(^3\text{LE}\) state or a combination of \(^3\text{LE}\) state and lo\(^{3}\)CT states (that is, \(^1\text{Cz}^+\) and \(^3\text{Cz}^+\)). This indicates, for CzBN derivatives, that neither the presence of only a \(^3\text{LE}\) state nor a combination of \(^3\text{LE}\) and de\(^{3}\)CT states is a sufficient condition for the activation of TADF, and instead, the presence of a de\(^{3}\)CT state is the key factor for increasing \(k_{\text{RISC}}\). The de\(^{3}\)CT facilitates RISC irrespective of \(\Delta E_{\text{ST}}\). However, this does not exclude the contribution of the combination of \(^3\text{LE}\) and \(^3\text{LE}\) states to \(k_{\text{RISC}}\) as 2CzPN, which showed these two states (Fig. 3B) has been reported to exhibit weak TADF (4.2 percentage point contribution to a total PLQY of 46%) (18). This result suggests that a combination of lo\(^{3}\)CT and \(^3\text{LE}\) states can also be essentially involved in the RISC process if a D unit is combined with a strong A unit, such as PN. That is, the stabilization of the CT state is an important factor for enhancing \(k_{\text{RISC}}\).

Now, the practically relevant question is what are the structural requirements for de\(^{3}\)CT formation? The TAS results of the CzBN derivatives demonstrated that the position of the Cz units connected to the BN core is important. Namely, the positioning of Cz moieties at 2 and 3 (2CzBN) or 2, 4, and 6 (p-3CzBN) cannot satisfy the structural requirement (see Fig. 1C). Although the Cz at the 4-position of o-3CzBN might be expected to tend to form \(^1\text{Cz}^+\) because of the low electron density, the TAS results showed that the Cz at the 4-position does not form a CR band with the neighboring Cz moieties at the 3- or 5-position. In addition, we confirmed that the Cz at the 2-position does not play a role in the CR band of p-3CzBN because movement of the Cz from 2- to 4-position in p-3CzBN also showed the CR band (fig. S5). Consequently, we identify the common structure among the
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 \( ^1\text{LE} \) and \( ^1\text{CT} \) \((25, 27)\). In addition, as Gibson et al. \((27)\) demonstrated theoretically, a vibronic coupling between the \( ^3\text{CT} \) and \( ^1\text{LE} \) 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 $^3\text{LE}$ level observed only for 2CzBN is used as a common one for all the CzBN derivatives because the $^3\text{LE}$, 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 $S_1$ state for the TADF-active molecules, in line with the formation of an ICT 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 p-3CzBN, ~4% at room temperature, made the comparison in the present stage difficult. The $k_{\text{RISC}}$ of 5CzBN is higher than that of 4CzBN despite the larger energy gap between $\text{de}^\text{exc}\text{CT}$ and $^3\text{LE}$ for 5CzBN than for 4CzBN. We speculate that the reason for this is effective vibronic coupling among $\text{de}^\text{exc}\text{CT}$, $^3\text{LE}$, and $^4\text{CT}$, as observed in the TAS of 5CzBN. An efficient vibronic coupling can occur between $^3\text{LE}$ and $^4\text{CT}$, but the coexistence of $\text{de}^\text{exc}\text{CT}$ may assist the vibronic coupling in 5CzBN.

Finally, we propose a comprehensive design strategy for TADF molecules to obtain a high PLQY. Although 4CzBN and 5CzBN exhibit comparable values that are one order of magnitude higher than the PLQY of 3LE, which originates from a phenyl-Cz, is not significantly affected by adding acceptor substituents (see the phosphorescence spectrum of 2CzBN and TCzB). It is seen that, although the $\Delta E_{\text{ST}}$ of the TADF-inactive molecules is similar to those reported by Uoyama et al. and Hosokai et al., the most rigid molecule, 5CzBN, shows the highest PLQY owing to the suppression of $\text{de}^\text{exc}\text{CT}$ 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 for future molecular light-emitting devices.

**MATERIALS AND METHODS**

**Materials**

4CzIPN, 2CzPN, 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 $<5 \times 10^{-5}$ Pa. After device fabrication, devices were immediately encapsulated with glass lids using epoxy glue in a nitrogen atmosphere.

The current density–voltage–luminance characteristics of the OLEDs were evaluated using a source measurement meter (B2912A, Agilent) and a calibrated spectroradiometer (CS-2000A, 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).
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 light 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 Nd: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 4CzPN 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 (CT2) 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.

REFERENCES AND NOTES
1. M. A. Baldo, D. F. O’Brien, M. E. Thompson, S. R. Forrest, Excitonic singlet-triplet ratio in a semiconductor-organic thin film. Phys. Rev. B 60, 14422–14428 (1999).
2. N. J. Turro, V. Ramamurthy, J. C. Scaino, Principle of Molecular Photochemistry: An Introduction (University Science Books, 2009), chap. 3, pp. 113–118.
3. Y. Kawamura, K. Goushi, J. Brooks, J. J. Brown, H. Sasabe, C. Adachi, 100% phosphorescence quantum efficiency of Ir (III) complexes in organic semiconductor films. Appl. Phys. Lett. 86, 071104 (2005).
4. C. Adachi, Third-generation organic electroluminescence materials. Jpn. J. Appl. Phys. 53, 060101 (2014).
5. H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 492, 234–238 (2012).
6. F. B. Dias, K. N. Bourdakos, V. Jankus, K. C. Moss, K. T. Kamtekar, V. Bahilla, J. Santos, M. P. Bryce, A. P. Monkman, Triplet harvesting with 100% efficiency by way of thermally activated delayed fluorescence in charge transfer OLED emitters. Adv. Mater. 25, 3707–3714 (2013).
7. J. W. Sun, J.-H. Lee, C. K. Moon, K.-H. Kim, H. Shin, J.-J. Kim, A fluorescent organic light-emitting diode with 30% external quantum efficiency. Adv. Mater. 26, 5684–5688 (2014).
8. Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, W. Huang, Thermally activated delayed fluorescence materials towards the breakthrough of organoelectronics. Adv. Mater. 26, 7931–7958 (2014).
9. S. Zhang, L. Yao, Q. Peng, W. Li, Y. Pan, R. Xiao, Y. Gao, C. Gu, Z. Wang, P. Lu, F. Li, S. Su, B. Yang, Y. Ma, Achieving a significantly increased efficiency in non-doped pure blue fluorescent OLED: A quasi-equivalent hybridized excited state. Adv. Funct. Mater. 25, 1755–1762 (2015).
10. D. R. Lee, M. Kim, S. K. Jeon, S.-H. Hwang, C. W. Lee, J. Y. Lee, Design strategy for 25% external quantum efficiency in green and blue thermally activated delayed fluorescent devices. Adv. Mater. 27, 5861–5867 (2015).
11. R. Komatsu, H. Sasabe, Y. Seino, K. Nakao, J. Kido, Light-blue thermally activated delayed fluorescent emitters realizing a high external quantum efficiency of 25% and unprecedented low drive voltages in OLEDs. J. Mater. Chem. C 4, 2274–2278 (2016).
12. C. Baleažio, M. N. Berberan-Santos, Thermally activated delayed fluorescence as a cycling process between excited singlet and triplet states: Application to the fullerenes. J. Chem. Phys. 126, 204510 (2007).
13. S. Y. Lee, T. Yasuda, H. Nomura, C. Adachi, High-efficiency organic light-emitting diodes utilizing thermally activated delayed fluorescence from triazene-based donor–acceptor hybrid molecules. Appl. Phys. Lett. 101, 093306 (2012).
14. T. Nakagawa, S. Y. Ku, K.-T. Wong, C. Adachi, Electroluminescence based on thermally activated delayed fluorescence generated by a spirofluorene donor-acceptor structure. Chem. Commun. 48, 9580–9582 (2012).
15. H. Tanaka, K. Shizu, H. Miyazaki, C. Adachi, Efficient green thermally activated delayed fluorescence (TADF) from a phenoxazine-triphenylamine (PKZ–TRZ) derivative. Chem. Commun. 48, 11392–11394 (2012).
16. K. Sato, K. Shizu, K. Yoshimura, A. Kawada, H. Miyazaki, C. Adachi, Organic luminescence molecule with energetically equivalent singlet and triplet excited states for organic light-emitting diodes. Phys. Rev. Lett. 110, 247401 (2013).
17. K. Nasu, T. Nakagawa, H. Nomura, C. Lin, C.-H. Chen, M.-R. Tseng, T. Yasuda, C. Adachi, A highly luminescent spiro-anthracenone-based organic light-emitting diode exhibiting thermally activated delayed fluorescence. Chem. Commun. 49, 10385–10387 (2013).
18. K. Masui, H. Nakanotani, C. Adachi, Analysis of exciton annihilation in high-efficiency sky-blue organic light-emitting diodes with thermally activated delayed fluorescence. Org. Electron. 14, 2721–2726 (2013).
19. T. Furukawa, H. Nakanotani, M. Inoue, C. Adachi, Dual enhancement of electroluminescence efficiency and operational stability by rapid upconversion of triplet excitons in OLEDs. Sci. Rep. 5, 8429 (2015).
20. D. D. Zhang, M. H. Cai, Y. G. Zhang, D. Q. Zhang, L. Duan, Sterically shielded blue thermally activated delayed fluorescence emitters with improved efficiency and stability. Mater. Horiz. 3, 145–151 (2016).
21. D. Zhang, M. Cai, Z. Bin, Y. Zhang, D. Luan, Highly efficient blue thermally activated delayed fluorescent OLEDs with record-low driving voltages utilizing high triplet energy hosts with small singlet-triplet splittings. Chem. Sci. 7, 3355–3363 (2016).
22. D. Y. Kondakov, T. D. Pawlik, T. K. Hatwar, J. P. Spindler, Triplet annealation exceeding spin statistical limit in highly efficient fluorescent organic light-emitting diodes. J. Appl. Phys. 106, 124510 (2009).
23. P. Data, P. Pander, M. Okazaki, Y. Takeda, S. Minakata, A. P. Monkman, Dibenzo[α,γ]phenazine-core donor–acceptor–donor compounds as green-to-red/NIR thermally activated delayed fluorescence organic light emitters. Angew. Chem. Int. Ed. Engl. 55, 5739–5744 (2016).
24. X.-K. Chen, S.-F. Zhang, J.-X. Fan, A.-M. Ren, Nature of highly efficiently thermally activated delayed fluorescent diodes in organic light-emitting diodes: Nonadiabatic effect between excited states. J. Phys. Chem. C 119, 9728–9733 (2015).
25. F. B. Dias, J. Santos, D. R. Graves, P. Data, R. S. Nobuyasu, M. A. Fox, A. S. Batsanov, T. Palmeira, M. N. Berberan-Santos, M. P. Bryce, A. P. Monkman, The role of local triplet excited states and D-A relative orientation in thermally activated delayed fluorescence: Photophysics and devices. Adv. Sci. 3, 1600080 (2016).
26. C. M. Marian, Mechanism of the triplet-to-singlet upconversion in the assistant dopant ACrXTN. J. Phys. Chem. C 120, 3715–3721 (2016).
27. J. Gibson, A. P. Monkman, T. J. Penfold, The importance of vibronic coupling for efficient reverse intersystem crossing in thermally activated delayed fluorescence molecules. ChemPhysChem 17, 2956–2961 (2016).
28. T. Yoshihara, M. Murai, Y. Tamaki, A. Furube, R. Kato, Trace analysis by transient absorption spectroscopy: Estimation of the solubility of CoO in polar solvents. Chem. Phys. Lett. 394, 161–164 (2004).
29. R. Katoh, A. Furube, N. Fuke, A. Fukui, N. Koide. Ultrafast relaxation as a possible limiting factor of electron injection efficiency in black dye sensitized nanocrystalline TiO2 films. J. Phys. Chem. C 116, 22301–22306 (2012).

30. S. Mahanta, A. Furube, H. Matsuzaki, T. N. Murakami, H. Matsumoto. Electron injection efficiency in Ru-dye sensitized TiO2 in the presence of room temperature ionic liquid solvents probed by femtosecond transient absorption spectroscopy: Effect of varying anions. J. Phys. Chem. C 116, 20213–20219 (2012).

31. M. Yamamoto, Y. Tsuji, A. Tsuchida. Near-infrared charge resonance band of intramolecular carbazole dimer radical cations studied by nanosecond laser photolysis. Chem. Phys. Lett. 154, 559–562 (1989).

32. B. R. Kaafarani, C. Risko, T. H. El-Assaad, A. O. El-Ballouli, S. R. Marder, S. Barlow. Mixed-valence cations of Di(carbazol-9-yl)biphenyl, tetrahydropryrene, and pyrene derivatives. J. Phys. Chem. C 120, 3156–3166 (2016).

33. T. Ogiwara, Y. Wakikawa, T. Ikoma. Mechanism of intersystem crossing of thermally activated delayed fluorescence molecules. J. Phys. Chem. A 119, 3415–3418 (2015).

34. Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki, C. Adachi. Design of efficient thermally activated delayed fluorescence materials for pure blue organic light emitting diodes. J. Am. Chem. Soc. 134, 14706–14709 (2012).

35. A. Heckmann, C. Lambert. Organic mixed-valence compounds: A playground for electrons and holes. Angew. Chem. Int. Ed. Engl. 51, 326–392 (2012).

Acknowledgments: We thank W. J. Potscavage Jr. for assistance with the preparation of this manuscript and T. Yoshioka for assistance with this project. Funding: This work was supported, in part, by the “Development of Fundamental Evaluation Technology for Next-Generation Chemical Materials” program commissioned by the New Energy and Industrial Technology Development Organization, and the International Institute for Carbon Neutral Energy Research (WPI-I2CNER) sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

Author contributions: T.H. and H.M. performed TAS measurements and T.H., H.M., A.F., and H. Nakanotani analyzed the data. T.H. and H. Nakanotani determined photophysical properties and analyzed the data. K.N. and H. Nomura prepared CzPN and CzBN derivatives. H. Nakanotani fabricated OLEDs and analyzed the data. T.H. and H. Nakanotani coordinated the work and wrote the paper. K.T., T.T., M.Y., and C.A. conceived the project, and all authors critically commented on the manuscript. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 26 December 2016
Accepted 9 March 2017
Published 10 May 2017
10.1126/sciadv.1603282

Citation: T. Hosokai, H. Matsuzaki, H. Nakanotani, K. Tokumaru, T. Tsutsui, A. Furube, K. Nasu, H. Nomura, M. Yahiro, C. Adachi, Evidence and mechanism of efficient thermally activated delayed fluorescence promoted by delocalized excited states. Sci. Adv. 3, e1603282 (2017).
Evidence and mechanism of efficient thermally activated delayed fluorescence promoted by delocalized excited states
Takuya Hosokai, Hiroyuki Matsuzaki, Hajime Nakanotani, Katsumi Tokumaru, Tetsuo Tsutsui, Akihiro Furube, Keirou Nasu, Hiroko Nomura, Masayuki Yahiro and Chihaya Adachi

Sci Adv 3 (5), e1603282.
DOI: 10.1126/sciadv.1603282