Thermally Activated Delayed Fluorescence Emitter with a Symmetric Acceptor–Donor–Acceptor Structure

Katsuyuki Shizu, Takuya Miwa, Yoshimasa Wada, Isamu Ogata, and Hironori Kaji*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

* kaji@scl.kyoto-u.ac.jp

A thermally activated delayed fluorescence (TADF) emitter with a symmetric acceptor–donor–acceptor structure, 3,3’-(9H,9’H-[3,3’-bicarbazole]-9,9’-diyl)bis(9H-xanthen-9-one) (CzX), was developed. Theoretical calculations based on quantum chemistry revealed that the energy difference between the singlet and triplet excited states of CzX was sufficiently small to allow TADF. In addition, the symmetric acceptor–donor–acceptor structure of CzX provided a widely distributed overlap density between its lowest singlet excited state and ground state, which led to a large transition dipole moment between them. These results suggested that CzX is promising as an efficient TADF emitter. An organic light-emitting diode (OLED) containing CzX as an emitting dopant was fabricated by vacuum deposition. The OLED displayed a maximum quantum efficiency of 19.9%. Such a high external quantum efficiency resulted from efficient TADF from CzX.

Keywords: Organic light-emitting diode, Thermally activated delayed fluorescence, Acceptor–donor–acceptor structure, Overlap density, Transition dipole moment

1. Introduction

Organic light-emitting diodes (OLEDs) [1,2] are light-emitting devices that contain layers of organic materials for light emission, carrier transport, carrier injection, and carrier generation. OLEDs make it possible to fabricate lightweight flat-panel displays with a wide viewing angle and fast response time. Smartphones and large-screen TVs with full-color OLED panels are commercially available. In addition to display applications, OLEDs have attracted great attention for use in next-generation solid-state lighting [3].

Under electrical excitation, singlet and triplet excitons are generated with a 1:3 ratio; that is, singlet and triplet excitons account for 25% and 75% of the total electrogenerated excitons, respectively. The light-emitting layer of an OLED typically contains host and emissive guest materials. Singlet and triplet excitons are generated and harvested on host molecules and then transferred to the emitting molecules, in which the excitons are converted into light. Therefore, the luminescence efficiency of OLEDs strongly depends on the efficiency that singlet and triplet excitons are converted into light by the emitting molecules.

![Fig. 1. Emission mechanisms of prompt and delayed fluorescence.](image-url)

Fig. 1. Emission mechanisms of prompt and delayed fluorescence. S₀, Sₙ (n=1, 2, ⋮) are the ground state, excited singlet states, and S₀, Sₙ (m=1, 2, ⋮) are the excited triplet states of a TADF emitter, respectively.

Recently, thermally activated delayed fluorescence (TADF) emitters have attracted renewed interest as emitting dopants for OLEDs because they can potentially convert all the electrogenerated singlet and triplet excitons into light [4-7]. In addition to converting singlet excitons into light as prompt fluorescence, TADF emitters can also convert triplet excitons into light through
delayed fluorescence (Fig. 1). This feature makes TADF emitters promising as emissive dopants for OLEDs. The lifetimes of prompt fluorescence ($\tau_p$) and delayed fluorescence ($\tau_d$) are typically nanosecond and micro- to millisecond order, respectively. The transient photoluminescence (PL) decay of an excited TADF emitter is therefore composed of rapid and slow decays corresponding to prompt fluorescence and delayed fluorescence, respectively. As a result, transient PL decay measurements provide insight into the emission mechanisms of TADF emitters.

The TADF efficiency depends on the efficiency of reverse intersystem crossing (RISC) from the excited triplet states $T_n$ of reverse intersystem crossing (RISC) from the mechanisms of TADF emitters. $\tau_p$ measurements provide insight into the emission respectively. As a result, transient PL decay composed of rapid and slow decays corresponding to prompt fluorescence and delayed fluorescence, respectively. Therefore, the HOMO and LUMO units have been used in various other TADF emitters.

From Eqs. 1 and 2, $|\mu_{\alpha0}|$ is large if $\rho_{\alpha0}(x)$ is mainly distributed in regions distant from the coordinate origin of a molecule [29-32]. For example, when $\rho_{\alpha0}(x)$ is large at large $y$, the product $\rho_{\alpha0}(x)(-ey)$ is a large negative or positive value at the point. Because the spatial integral of $\rho_{\alpha0}(x)(-ey)$ gives $(\mu_{\alpha0})_y$, if $\rho_{\alpha0}(x)$ is widely distributed in regions where $y$ is large, $(\mu_{\alpha0})_y$ has a large negative or positive value, leading to a large $|\mu_{\alpha0}|$:

$$|\mu_{\alpha0}| = \sqrt{|(\mu_{\alpha0})_x|^2 + |(\mu_{\alpha0})_y|^2 + |(\mu_{\alpha0})_z|^2} \quad (3)$$

This idea holds for $(\mu_{\alpha0})_x$ and $(\mu_{\alpha0})_z$ as well. Thus, extending the $\rho_{\alpha0}(x)$ distribution to regions distant from the coordinate origin of a molecule is an effective way to increase $|\mu_{\alpha0}|$ and improve luminescence efficiency [29-32]. According to Kasha’s rule, fluorescence occurs between $S_1$ and $S_0$, so $|\mu_{\alpha0}|$ is the most important transition dipole moment. When the HOMO–LUMO excitation predominantly contributes to the electronic configuration of $\Phi_0(x)$, the spatial overlap between the HOMO and LUMO dominates the $\rho_{10}(x)$ distribution. Therefore, extending HOMO and/or LUMO distributions to regions distant from the coordinate origin is a suitable approach to increase $|\mu_{10}|$.

In this study, we develop a TADF emitter with a symmetric acceptor–donor–acceptor structure, 3,3’- (9H,9’H-[3,3’-bicarbazole]-9,9’-diyl)bis(9H-xanthen-9-one) (CzX, Figure 2). The 3,3’-bicarbazole-based group of CzX acts as an electron-donating moiety and the two 9H-xanthen-9-one-based ones act as electron-accepting moieties. Both 3,3’-bicarbazole [19-24] and 9H-xanthen-9-one [25-28] units have been used in various other TADF emitters.

Quantum chemical calculations suggest that $\Delta E_{ST}$ values of CzX are sufficiently small for TADF. Furthermore, the symmetric acceptor–donor–acceptor structure effectively extends its $\rho_{10}(x)$ distribution and leads to a large $|\mu_{10}|$. When doped into a host material, CzX is found to emit delayed fluorescence. An OLED containing CzX as an emitting dopant shows a maximum external quantum efficiency (EQE) of 19.9%.

2. Method to calculate singlet and triplet excited states of CzX

Figure 2 shows the $S_0$ geometries of two rotational isomers of CzX, labeled CzX-A and CzX-B. The geometries were optimized using density functional theory (DFT) at the PBE0/6-31G(d) level of theory assuming $C_s$ and $C_2$ symmetries for CzX-A and CzX-B, respectively. The stability of the
optimized geometries was confirmed from frequency calculations performed at the PBE0/6-31G(d) level of theory. For CzX-A and CzX-B, the torsion angles between the central carbazole units were calculated to be 39.5° and 37.4°, respectively. The DFT calculations revealed that CzX-A was more energetically stable than CzX-B by 0.0775 kcal/mol (3.36 meV).

Electronic excited states of CzX-A and CzX-B were calculated using the 6-31+G(d) basis set, a long-range corrected density functional called LC-ωPBE [33], and the time-dependent DFT (TD-DFT) method within the Tamm–Dancoff approximation (TDA) [34]. LC-ωPBE is designed to describe CT excitation energies, of which the electron-repulsion operator is divided into short- and long-range terms:

\[ \frac{1}{|r_{12}|} = \frac{1 - \text{erf}(\omega |r_{12}|)}{|r_{12}|} + \text{erf}(\omega |r_{12}|), \]

where erf denotes the standard error function, ω is a parameter that defines the range separation, and |r_{12}| is the distance between electrons. When the optimal ω (denoted as ω*) is used, the LC-ωPBE/6-31+G(d) method can reliably predict ΔE_{ST} for a series of TADF emitters [35]. ω* was optimized by minimizing J^2:

\[ J^2 = \sum_{i=0}^{N} \varepsilon \text{(N+i)} + \text{IP(N+i)}^2, \]

where N is the number of electrons of neutral CzX, and ε and IP are the HOMO/singly occupied molecular orbital and ionization potential of CzX with N/N+1 electrons, respectively. For CzX-A and CzX-B, ω* was determined to be 0.171 Bohr\(^{-1}\), which is less than half the default ω value of 0.400 Bohr\(^{-1}\). The method of calculating excited states using the optimal ω is denoted as TDA-LC-ωPBE/6-31+G(d). Twenty low-lying excited singlet and triplet states (S\(_1\)–S\(_{20}\) and T\(_1\)–T\(_{20}\)) of CzX-A and CzX-B in toluene solution were calculated using the S\(_0\) geometries optimized at the PBE0/6-31+G(d) level of theory, TDA-LC-ωPBE/6-31+G(d) method, and polarizable continuum model (PCM) [36]. All the quantum chemical calculations were performed using the Gaussian 09 program package [37].

3. Molecular design of CzX

Fig. 3 shows the calculated S\(_0\)→S\(_n\) (n = 1, 2, 3, 4) and S\(_0\)→T\(_m\) (m = 1, 2, ···, 10) excitation energies (ΔE) of CzX-A and CzX-B, revealing that CzX-A and CzX-B show similar ΔE. In the following, we focus on the excited-state properties of CzX-A. S\(_1\)–S\(_4\) of CzX-A are close in energy and its T\(_1\)–T\(_{10}\) lie between S\(_0\) and S\(_1\). ΔE_{ST} between S\(_1\) and T\(_{m}\) (m = 1, 2, ···, 10) ranges from 2 to 403 meV. Although a ΔE_{ST} of 403 meV is relatively large, it is comparable to that of a highly efficient blue TADF emitter containing a 3,3’-bicarbazole-based electron-donating moiety, 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-9’-phenyl-9H,9’H-3,3’-bicarbazole (BCzT) [31]: ΔE_{ST} between S\(_1\) and T\(_1\) of BCzT was calculated to be 409 meV using the same theoretical method (ω* = 0.162 Bohr\(^{-1}\)). This result suggests that the ΔE_{ST} values of CzX are sufficiently small to allow efficient TADF.
Table 1. Low-lying excited states of CzX-A calculated using the TDA-LC-ω*PBE/6-31+G(d) and PCM methods. H and L denote HOMO and LUMO, respectively. Numbers in parentheses are $\Delta E$ in nm.

| State | $\Delta E$ (eV) | $|\mu|_0$ (a.u.) | Dominant configuration |
|-------|----------------|-----------------|-----------------------|
| S₁    | 3.507          | 3.363           | H → L 49.5%           |
|       | (354)          |                 | H−1 → L+1 20.0%       |
|       |                 |                 | H−7 → L+1 7.1%        |
|       |                 |                 | H−6 → L 6.7%          |
| S₂    | 3.541          | 0.188           | H−7 → L 35.4%         |
|       | (350)          |                 | H−6 → L+1 34.6%       |
|       |                 |                 | H → L+1 15.2%         |
|       |                 |                 | H−1 → L 7.2%          |
| S₃    | 3.562          | 1.477           | H−6 → L 41.1%         |
|       | (348)          |                 | H−7 → L+1 41.0%       |
|       |                 |                 | H → L 8.2%            |
|       |                 |                 | H−1 → L+1 3.3%        |
| S₄    | 3.587          | 0.281           | H−1 → L 19.6%         |
|       | (346)          |                 | H−6 → L+1 13.2%       |
|       |                 |                 | H−7 → L 12.8%         |

$AE$ and dominant electronic configurations of S₁–S₄ are listed in Table 1. $AE$ ranges from 3.507 to 3.587 eV (corresponding to 346 to 354 nm). Figure 4 depicts ultraviolet–visible (UV-vis) absorption and PL spectra for CzX in toluene solution. The peak wavelength of the first absorption band is 375 nm, which is approximately 20 nm longer than the calculated value of 354 nm. CzX exhibited blue emission and a photoluminescence quantum yield (PLQY) of 54% in dilute toluene solution.

Fig. 5. LUMO, LUMO+1, HOMO, HOMO−1, HOMO−6, and HOMO−7 of CzX calculated using the LC-ω*PBE/6-31+G(d) and PCM methods.

Four occupied molecular orbitals, HOMO, HOMO−1, HOMO−6, and HOMO−7 and two unoccupied molecular orbitals, LUMO and LUMO+1, predominantly contribute to the electronic configuration of S₁–S₄. Figure 5 shows these six molecular orbitals of CzX-A calculated using the LC-ω*PBE/6-31+G(d) and PCM methods. HOMO and HOMO−1 are distributed predominantly on the electron-donating moiety, while HOMO−6, HOMO−7, LUMO, and LUMO+1 are distributed predominantly on the electron-accepting moieties. Thus, the HOMO → LUMO, HOMO → LUMO+1, HOMO−1 → LUMO, and HOMO−1 → LUMO+1 excitations have CT character: upon excitation, an electron transfers from the electron-donating moiety to the electron-accepting moieties. Meanwhile, the HOMO−7 → LUMO, HOMO−7 → LUMO+1, HOMO−6 → LUMO, and HOMO−6 → LUMO+1 excitations are localized on the electron-accepting moieties and have the $n-\pi^*$ character of the carbonyl groups. From Table 1 and Figure 5, S₁ and S₄ are CT excited sates, while S₂ and S₃ are locally excited (LE) states. However, the $n-\pi^*$ and CT excitations make non-negligible contributions to the CT-excited and LE states, respectively. From the theoretical calculations, T₁ also has CT character: the HOMO → LUMO and HOMO → LUMO+1 excitations make the largest and second largest contributions to the electronic configurations of T₁, respectively. The CT character of T₁ and S₁ results in the small $\Delta E_{ST}$ between them.
transition dipole moments that represented the spatial distribution of especially in the direction of the regions distant from the coordinate origin. Because the spatial integral of regions of the electron-accepting moieties (Figure 6b) are 0.0004 and 0.001 a.u., respectively (light grey regions: positive; gray regions: negative). Atomic transition dipole moments with respect to\(\mu_{10}\) of CzX in a.u. Atomic transition dipole moments on the electron-donating moieties are small compared with those on the electron-accepting one. This is because the electron-donating moiety is more closely located around the coordinate origin. Thus, the symmetric acceptor–donor–acceptor structure extends the\(\rho_{10}(x)\) distribution to regions distant from the coordinate origin and provides CzX with its large \(|\mu_{10}|\).

4. Transient PL decay measurements and device performance of CzX

To confirm delayed fluorescence from CzX, we measured the transient PL decay properties of a 6 wt% CzX-doped dibenzo\([b,d]\)furan-2,8-diylbis(diphenylphosphine oxide) (PPF) film. Figure 7a shows temperature dependence of the PL decay curve of the doped film. The delayed component measured at 300 K is larger than that measured at 200 K, which is probably caused by TADF from CzX. An OLED containing a 6 wt% CzX-doped PPF layer as an emitting layer was fabricated by vacuum deposition. The device structure was indium tin oxide (50 nm)/4,4’- (cyclohexane-1,1-diyl)-bis(\(N,N\text{-di-p-tolylaniline})\) (60 nm)/4,4’-bis(\(N\text{-carbazolyl})-1,1’-biphenyl (10 nm)/6 wt% CzX-doped PPF (30 nm)/PPF (10 nm)/3,3’’\(,5,5’’\text{-tetra(pyridin-3-yl)-1,1’\text{-3’},1’’\text{-terphenyl}}\) (30 nm)/lithium quinolin-8-olate (1 nm)/Al (80 nm). Figure 7b displays the EQE–luminance characteristics of the OLED. The OLED showed a maximum EQE of 19.9%. This high EQE is attributed to efficient TADF from CzX. The peak of its EL spectrum was located at 482 nm, which was 30 nm longer than that of the PL spectrum for CzX in toluene solution (Figure 4). The Commission Internationale d’Enclairage coordinates of the device were (0.18, 0.32) at a current density of 10 mA cm\(^{-2}\).
Fig. 7. (a) Transient PL decay curves of a 6 wt% CzX-doped PPF film. (b) EQE–luminance characteristics of a CzX-based OLED. The inset is its EL spectrum measured at 10 mA cm⁻².

5. Experimental

Scheme 1 shows the synthetic route to CzX [¹H NMR (600 MHz, CDCl₃): δ 8.62 (d, J = 8.2 Hz, 2H), 8.49 (d, J = 2.1 Hz, 2H), 8.42 (dd, J = 1.4, 8.2 Hz, 2H), 8.27 (d, J = 6.9 Hz, 2H) 7.84 (m, 4H), 7.79 (m, 2H), 7.73 (dt, J = 2.1, 8.2 Hz, 4H), 7.66 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H), 7.51 (m, 2H), 7.46 (m, 2H), 7.4 (t, J = 7.2 Hz, 2H)]. The ¹H NMR spectrum of CzX was recorded using a 600-MHz spectrometer (ECA-600, JEOL, Japan). UV-vis and PL spectra were measured using a UV-vis spectrophotometer (UV-3150, Shimadzu, Japan) and spectrofluorometer (Fluoromax-4P, Horiba, Japan), respectively. The excitation wavelength was 375 nm. PLQY was measured using an absolute PLQY spectrometer (Quantaurus-QY C11347-01, Hamamatsu Photonics, Japan). Transient PL decay curves were obtained using a fluorescence lifetime spectrometer (Quantaurus-Tau C11367-01, Hamamatsu Photonics, Japan). OLED characteristics were measured using a source meter (2400, Keithley, Japan) and an absolute EQE measurement system with an integrating sphere (C9920-12, Hamamatsu Photonics, Japan).

6. Conclusion

We developed the acceptor–donor–acceptor-type TADF emitter, CzX. Theoretical calculations based on quantum chemistry indicated that the symmetric acceptor–donor–acceptor structure of CzX provided it with a sufficiently small S₁–T₁ energy gap and large transition dipole moment between S₁ and S₀, which are desirable properties for efficient TADF. CzX exhibited blue emission in dilute toluene solution and delayed fluorescence when doped into PPF. An OLED containing CzX-doped PPF as an emissive layer exhibited a maximum EQE of 19.9%. This value is much higher than that obtained with normal fluorescent emitters. The efficient TADF from CzX was responsible for the high EQE of its OLED.

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References
