Efficient emitting molecules in organic light-emitting diodes on the basis of the control of vibronic couplings

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Abstract. A high external quantum efficiency observed in organic light-emitting diodes using PTZ-BZP (PTZ: 10-hexyl-phenothiazin, and BZP: 4-phenyl-2,1,3-benzothiadiazole) as an emitting molecule is studied based on the vibronic coupling density analyses employing the time-dependent density functional theory. The high efficiency can be attributed to a high efficiency of exciton generation which originates from reverse intersystem crossings from the higher $T_3$ and $T_2$ states than $T_1$ to the emitting $S_1$ state. The nonradiative transitions from $T_3$ and $T_2$ to the lower triplet states are suppressed because of small off-diagonal vibronic coupling constants. The small vibronic couplings originate from the multi-configurationality of these triplet states. A molecular design principle for efficient emitting molecules is discussed from the view of the control of vibronic couplings.

1. Introduction

Vibronic couplings play important roles in light emission from a molecule. Off-diagonal vibronic couplings give rise to nonradiative transitions, and diagonal vibronic couplings are related to the geometrical deviation of the minimum of the ground and excited state[1]. A large vibrational relaxation results in small Franck-Condon factors which give rise to a small rate constant of the radiative transition. Therefore, small diagonal and off-diagonal vibronic couplings are crucial in designing of an efficient emitting molecule.

We have proposed concepts of vibronic coupling densities (VCD) to analyze and control diagonal and off-diagonal vibronic couplings[2, 3]. On the basis of vibronic coupling density analysis, we designed efficient emitting molecules by the suppression of vibronic couplings in anthracene[4] and triphenylamine[5], and we experimentally observed the increases of quantum yields of the designed molecules[6, 7]. It should be noted that triphenylamine is known as a non-emitting molecule. We can make a non-emitting molecule fluorescent by a molecular design on the basis of a vibronic coupling density analysis.

Thermally-activated delayed fluorescence (TADF) has attracted much attention as a highly-efficient emitting mechanism for organic light-emitting diodes (OLED) [8, 9, 10, 11]. Thermally excited $T_1$ excitons are converted to $S_1$ excitons via reverse intersystem crossing. While a fluorescent OLED and a phosphorescent OLED utilize 25% singlet and 75% triplet excitons...
at best, respectively, in TADF OLED, both T$_1$ and S$_1$ excitons which are generated by current excitations are utilized for light emission. The external quantum efficiency (EQE) of a fluorescent, phosphorescent, and TADF OLED is 0.05 of photoluminescence quantum yield (PLQY), 0.15 of PLQY, and 0.20 of PLQY, respectively.

We have proposed a fluorescence via higher triplets mechanism to increase the efficiency of exciton generation[12, 13, 14]. Fluorescence via reverse intersystem crossing from T$_n$ states higher than T$_1$ to S$_m$ is possible by suppressing non-radiative transitions from T$_n$ based on the concept of vibronic coupling density as long as the energy level of T$_n$ is close to S$_m$.

Figure 1. Molecular structure of PTZ-BZP. PTZ-BZP consists of the central 10-hexyl-phenothiazin (PTZ) moiety and the two 4-phenyl-2,1,3-benzothiadiazole (BZP) moieties.

PTZ-BZP (see figure 1) consists of the central 10-hexyl-phenothiazin (PTZ) moiety and the two 4-phenyl-2,1,3-benzothiadiazole (BZP) moieties. Yao et al. have reported that they observed the electroluminescence (EL) of a device using PTZ-BZP as an emitting molecule with EQE=1.54 %[15]. Since the observed PLQY was 16%, we cannot explain the observed EQE based on the fluorescent EL mechanism. In other word, triplet excitons as well as singlet ones should be utilized in this device. In this study, we analyze the EL mechanism on the basis of VCD to elucidate the high efficiency of exciton generation in the OLED of PTZ-BZP employing the time-dependent density functional theory (TD-DFT). We also propose a molecular design principle for the fluorescence via higher triplets mechanism.

2. Vibronic coupling constants and vibronic coupling density
The definitions of vibronic coupling constants and vibronic coupling densities are briefly summarized here. See details in the literature[2, 3]. Vibronic coupling operator is written as

\[ \hat{V}Q_\alpha = \left( \frac{\partial \hat{H}}{\partial Q_\alpha} \right) R_0, \]  

where \( \hat{H} \) is a molecular Hamiltonian, \( Q_\alpha \) is the normal coordinate of mode \( \alpha \), and \( R_0 \) is a reference molecular geometry.

Diagonal vibronic coupling constant (VCC) of state \( n \) is defined by

\[ V_n^\alpha := \langle \Psi_n(R_0, r) | \hat{V}_\alpha | \Psi_n(R_0, r) \rangle + \left( \frac{\partial U_{nn}}{\partial Q_\alpha} \right) R_0, \]  

where \( \Psi_n(R_0, r) \) is the electronic wavefunction of state \( n \), and \( U_{nn} \) is the nuclear-nuclear repulsion. \( r \) denotes the coordinates of electrons. A diagonal VCC is the driving force of a
vibrational relaxation. The reorganization energy can be expressed in terms of diagonal VCCs,

\[ E_{\text{reorg}}^n = \sum_{\alpha} \left( \frac{V_{\alpha}^n}{2\omega_{\alpha}^2} \right)^2. \]  

(3)

Offdiagonal VCC between state \( m \) and \( n \) is defined by

\[ V_{mn}^\alpha := \langle \Psi_m(R_0, r) | \hat{V}_{\alpha} | \Psi_n(R_0, r) \rangle \]  

(4)

A offdiagonal VCC is a driving force of a nonradiative transition. Small offdiagonal VCCs result in the suppression of a nonradiative transition.

Offdiagonal vibronic coupling density (VCD) is defined by

\[ \eta_{mn}^\alpha (r_1) := \rho_{mn}(r_1) v^\alpha (r_1). \]  

(5)

VCD describes a local picture of a vibronic coupling (see Appendix). Potential derivative \( v^\alpha (r_1) \) is defined in Appendix, and overlap density \( \rho_{mn}(r_1) \) is defined by

\[ \rho_{mn}(r_1) := N \int \cdots \int d\sigma_1 d\sigma_2 \cdots d\sigma_N \Psi_m^*(R_0, x_1, \cdots, x_N) \Psi_n(R_0, x_1, \cdots, x_N), \]  

where \( x_i = (r_i, \sigma_i) \) with the space coordinates \( r_i \) and spin coordinate \( \sigma_i \) of electron \( i \). Offdiagonal VCC \( V_{mn}^\alpha \) is the integral of offdiagonal VCD \( \eta_{mn}^\alpha (r_1) \):

\[ V_{mn}^\alpha = \int \eta_{mn}^\alpha (r_1) dr_1. \]  

(7)

3. Method of calculation

The ground state was optimized employing M06-2X/6-31G(d,p). The semi-empirical functional M06-2X[16] has been employed in theoretical studies on TADF molecules[9]. The optimized structure of \( S_0 \) was confirmed by performing vibrational analysis. The excited states, \( S_1 \), \( T_1 \), \( T_2 \), and \( T_3 \) were optimized by using time-dependent density functional theory (TD-DFT) at the M06-2X/6-31G(d,p) level of theory. In our preliminary investigation at the B3LYP/6-31G(d,p) level of theory[13], the calculated absorption wavelength is too long compared with the experimental value[15].

The offdiagonal vibronic coupling constants and vibronic coupling densities were calculated from the excited electronic wavefunction for the optimized geometries. These electronic and vibrational structures were obtained by Gaussian09[17]. The VCC calculations and VCD analyses were performed by using our in-house codes. The vibrational vectors employed for the VC calculations and analyses were obtained from the vibrational analysis for the \( S_0 \) states at the optimized geometries of the excited states, since only a numerical frequency analysis is available for an excited state in Gaussian09. A numerical frequency analysis is computationally very demanding.

4. Results and discussion

4.1. Franck-Condon \( S_1 \) state

Table 1 summarizes the Franck-Condon excited states \( S_n \oplus S_0 \) and \( T_n \oplus S_0 \), where \( \oplus S_n \) means that the excited states are calculated for the \( S_0 \) optimized geometry. The calculated excitation energy of \( S_1 \) reproduces the experimental absorption wavelength well.

The calculated diagonal VCCs are shown in figure 2 for the vibrational modes. A large reorganization energy, or vibrational relaxation of \( S_1 \) suppresses the rate constant of a fluorescent process[1]. The total reorganization energy was estimated to be 372 meV by using Eq.(3), which is not so large as an emitting molecule[1].
Table 1. Franck-Condon excited states calculated at the M06-2X/6-31G(d,p) level of theory.

| State   | Excitation energy (eV) | nm  | f     | Major configurations (CI coefficient) |
|---------|------------------------|-----|-------|--------------------------------------|
| T₁ (³A) | 2.3225                 | 533.85 | 0.0000 | NHO → NLU (0.43658)                  |
|         |                        |      |       | HO → LU (0.35711)                    |
| T₂ (³A) | 2.3308                 | 531.94 | 0.0000 | NHO → LU (0.41920)                  |
|         |                        |      |       | HO → NLU (0.33955)                   |
| S₁ (¹A) | 3.2051                 | 386.83 | 0.7867 | HO → LU (0.59349)                    |
| T₃ (³A) | 3.2794                 | 378.07 | 0.0000 | HO → LU (0.36497)                    |
|         |                        |      |       | HO → LU+2 (0.32673)                  |
| S₂ (¹A) | 3.3470                 | 370.43 | 0.1971 | NHO → LU (0.30039)                  |
|         |                        |      |       | HO → NLU (0.58363)                   |
| Exp[15] | 2.77                   | 447 |       |                                       |

Figure 2. Diagonal vibronic coupling constants for the Franck-Condon S₁ state at the M06-2X/6-31G(d,p) level of theory.

4.2. S₁ adiabatic state
The excited states for the optimized structure of the S₁ state are tabulated in table 2. The energy levels of T₂ and T₃ are close to that of S₁. This suggests that the reverse intersystem crossing from T₂ or T₃ to S₁ could be possible if the energy levels of T₂@T₂ and S₁@T₂, or those of T₁@T₁ and S₁@T₁ are close each other with the offdiagonal VCCs between the higher triplet states and the lower ones small.

Offdiagonal vibronic couplings between S₁ and S₀ should be small as a fluorescent molecule. The offdiagonal VCCs between the S₁@S₁ and S₀@S₁ are shown in figure 3. They are less than 1 × 10⁻³ a.u. which is typical in a fluorescent molecule. The strong coupling modes are 7.29 × 10⁻⁴ a.u. of mode 111 (960 cm⁻¹) and 7.14 × 10⁻⁴ a.u. of mode 45 (403 cm⁻¹). We performed the VCD analyses for these modes.

Figure 4 shows the VCD analyses of the strong coupling modes, mode 111 and mode 45, for the S₁ adiabatic state. The overlap density between S₁@S₁ and S₀@S₁ is localized on the one
Table 2. $S_1$ adiabatic excited states calculated at the M06-2X/6-31G(d,p) level of theory.

| State       | Excitation energy | $f$ | Major configurations (CI coefficient)          |
|-------------|-------------------|-----|-----------------------------------------------|
| $T_1 (^3A)$ | 1.5619 eV         | 0.0000 | NHO $\rightarrow$ LU (0.42818)              |
|             | 793.81 nm         |     | HO $\rightarrow$ LU (0.51651)                |
| $T_2 (^3A)$ | 2.2316 eV         | 0.0000 | HO-2 $\rightarrow$ NLU (0.40509)            |
|             | 555.58 nm         |     | NHO $\rightarrow$ NLU (-0.30471)            |
|             |                   |     | HO $\rightarrow$ NLU (0.38302)              |
| $S_1 (^1A)$ | 2.4851 eV         | 0.6998 | HO $\rightarrow$ LU (0.66212)                |
| $T_3 (^3A)$ | 2.6813 eV         | 0.0000 | NHO $\rightarrow$ LU (0.34910)              |
|             | 462.40 nm         |     | HO $\rightarrow$ LU (-0.34410)              |
| $S_2 (^1A)$ | 3.0121 eV         | 0.2710 | HO $\rightarrow$ NLU (0.62714)               |
| Exp[15]     | 2.10              | 590  |                                               |

Figure 3. Offdiagonal vibronic coupling constants between $S_1$ and $S_0$ states for the adiabatic $S_1$ state at the M06-2X/6-31G(d,p) level of theory.

4.3. $T_3$ adiabatic state

The excited states for the optimized geometry of $T_3$ is summarized in table 3. The energy level of $T_3$ is close to that of $S_1$. The energy gap between $S_1$ and $T_3$, $\Delta E_{S_1@T_3 - T_3@T_3} = 25$ meV. This small energy gap makes the thermal activation from $T_3$ to $S_1$ possible if the offdiagonal vibronic couplings are small.

Figures 5 and 7 show the offdiagonal VCCs between the $T_3$ and $T_2$ states, and the $T_3$ and $T_1$ states, respectively. The strong coupling modes between $T_3$ and $T_2$ are $3.20 \times 10^{-4}$ a.u. of mode 201 (1629 cm$^{-1}$), and $-2.87 \times 10^{-4}$ a.u. of mode 177 (1420 cm$^{-1}$). The strong coupling modes between $T_3$ and $T_1$ are $3.62 \times 10^{-4}$ a.u. of mode 78 (697 cm$^{-1}$), and $3.11 \times 10^{-4}$ a.u. of the BZP moieties. As shown in figure 4 (c) and (e), therefore, the VCs originate from the overlap density on the BZP moiety. Accordingly, in order to enhance the PLQY, the overlap density on the BZP moiety should be reduced.
Figure 4. The VCD analyses for the $S_1$ adiabatic state at the M06-2X/6-31G(d,p) level of theory. Mode 111 and mode 45 indicate strong couplings. (a) Overlap density between $S_1@S_0$ and $S_0@S_1$, $\rho_{10}$, (b) potential derivative of mode 111, $v^{111}$, (c) VCD of mode 111, $\eta_{10}^{111}$, (d) potential derivative of mode 45, $v^{45}$, and (e) VCD of mode 45, $\eta_{10}^{45}$. The isosurface values are 5.0 x 10^-4 for $\rho$, 0.004 for $v$, and 5.0 x 10^-6 for $\eta$, respectively.

Table 3. $T_3$ adiabatic excited states calculated at the M06-2X/6-31G(d,p) level of theory.

| State | Excitation energy (eV) | Excitation energy (nm) | $f$ | Major configurations (CI coefficient) |
|-------|------------------------|------------------------|-----|--------------------------------------|
| $T_1$ ($^{3A}$) | 2.0115 | 616.39 | 0.0000 | NHO $\rightarrow$ NLU (-0.36213) |
|        |           |          |      | HO $\rightarrow$ LU (0.47322)      |
|        |           |          |      | HO-2 $\rightarrow$ LU (0.24834)    |
| $T_2$ ($^{3A}$) | 2.0799 | 596.09 | 0.0000 | NHO $\rightarrow$ LU (0.41808)      |
|        |           |          |      | HO $\rightarrow$ NLU (-0.40890)    |
|        |           |          |      | HO-2 $\rightarrow$ NLU (-0.29704)  |
| $T_3$ ($^{3A}$) | 2.6324 | 471.00 | 0.0000 | HO $\rightarrow$ LU+2 (0.39798)    |
|        |           |          |      | HO-2 $\rightarrow$ LU (0.28310)    |
|        |           |          |      | NHO $\rightarrow$ NLU (-0.25387)  |
|        |           |          |      | HO $\rightarrow$ NLU (-0.28352)    |
| $S_1$ ($^{1A}$) | 2.6574 | 466.56 | 0.6657 | HO $\rightarrow$ LU (0.65139)      |
| $S_2$ ($^{1A}$) | 2.9119 | 425.79 | 0.1057 | HO $\rightarrow$ NLU (0.66925)    |

of mode 202 (1630 cm$^{-1}$). These coupling constants are rather small, which suggests that the nonradiative transitions from the $T_3$ state to the $T_2$ and $T_1$ states are suppressed.

4.4. $T_2$ adiabatic state

Table 4 summarizes the excited states for the $T_2$ optimized geometry. The energy gap between the $T_2@T_2$ and $S_1@T_2$ states, $\Delta E_{S_1@T_2-T_2@T_2}$ is equal to -14.9 meV. If the offdiagonal vibronic couplings between $T_2$ and $T_1$ are small, the reverse intersystem crossing from $T_2$ to $S_1$ is possible.
The offdiagonal VCCs between the $T_2$ and $T_1$ states are shown in Figure 7. It should be noted that the order of the coupling constants is of $10^{-5}$ a.u. The extremely small coupling constants originate from the small overlap density discussed in the following subsection.

4.5. Reductions of the overlap densities
Figure 8 shows the overlap densities between the $T_3$ and $T_2$ states, the $T_3$ and $T_1$ states, and the $T_2$ and $T_1$ states. Note that the isosurface value (0.0005) of the overlap density between $S_1$ and $S_0$ shown in Figure 4 (a) is larger than the isosurface values (0.0002) of Figure 8. The overlap densities between the $T_3$ and $T_2$ states (Figure 8 (a)), and the $T_3$ and $T_1$ states (figure
Table 4. $T_2$ adiabatic excited states calculated at the M06-2X/6-31G(d,p) level of theory.

| State | Excitation energy (eV) | Excitation energy (nm) | $f$ | Major configurations (CI coefficient) |
|-------|------------------------|------------------------|------|--------------------------------------|
| $T_1$ ($^3A_1$) | 1.0565 | 1173.56 | 0.0000 | NHO $\rightarrow$ LU (0.35875) |
|       |           |              |      | HO $\rightarrow$ LU (0.60451)      |
| $S_1$ ($^1A_1$) | 2.3072 | 537.38 | 0.6700 | HO $\rightarrow$ LU (0.67479) |
| $T_2$ ($^3A_2$) | 2.3221 | 533.94 | 0.0000 | HO-2 $\rightarrow$ NLU (0.42305) |
|       |           |              |      | NHO $\rightarrow$ NLU (-0.39498)   |
| $T_3$ ($^3A_2$) | 2.7331 | 453.64 | 0.0000 | NHO $\rightarrow$ LU (0.42675) |
|       |           |              |      | HO $\rightarrow$ LU (-0.31247)     |
| $T_4$ ($^3A_2$) | 3.1743 | 390.58 | 0.0000 | HO-10 $\rightarrow$ LU (0.50716)   |
|       |           |              |      | HO-9 $\rightarrow$ LU (0.34630)    |
| $S_2$ ($^1A_1$) | 3.1799 | 389.90 | 0.2617 | NHO $\rightarrow$ LU (0.42893) |
|       |           |              |      | HO $\rightarrow$ NLU (-0.40933)    |

Figure 7. Offdiagonal vibronic coupling constants between $T_2$ and $T_1$ states for the adiabatic $T_2$ state at the M06-2X/6-31G(d,p) level of theory.

8 (b)) are reduced compared with that between the $S_1$ and $S_0$ states (figure 4 (a)). The overlap density between the $T_2$ and $T_1$ states (figure 8 (c)) are much reduced.

Compared with offdiagonal vibronic couplings between $S_1$ and $S_0$, which is a driving force of the nonradiative transition that competes with the fluorescent process, those between the higher triplet states and lower triplet ones are small in PTZ-BZP. This is one of the necessary condition for the fluorescence via higher triplets mechanism. We discuss this reductions from the view of the structures of the excited wave functions.

Overlap density between states $\Psi_1 = c_{1a}\Phi_a + c_{1b}\Phi_b$ and $\Psi_2 = c_{2c}\Phi_c + c_{2d}\Phi_d$, $\rho(\Psi_1, \Psi_2)$, can be expanded as a sum of the overlap densities between electronic configurations (Slater determinants):

$$\rho(\Psi_1, \Psi_2) = c_{1a}^* c_{2c}\rho(\Phi_a, \Phi_c) + c_{1a}^* c_{2d}\rho(\Phi_a, \Phi_d) + c_{1a}^* c_{2c}\rho(\Phi_a, \Phi_c) + c_{1a}^* c_{2d}\rho(\Phi_a, \Phi_d), \quad (8)$$
where $\Phi_i (i = a, b, c, d)$ is an electronic configuration, and $c_{ki} (k = 1, 2)$ is a configuration interaction (CI) coefficient.

A TD-DFT wavefunction consists of one-electron excited electronic configurations, $\Psi_i$, where $i$ denotes an occupied molecular orbital $\psi_i$, and $r$ is an unoccupied molecular orbital $\psi_r$:

$$\Psi = \sum c_i^r \Phi_i^r.$$  \hfill (9)

Overlap density between the electronic configurations satisfies the following:

$$\rho(\Phi_i^r, \Phi_j^s) = \rho_{0} - \rho_i + \rho_j,$$  \hfill (10)

$$\rho(\Phi_i^r, \Phi_j^r) = \psi_i^r \psi_j^r,$$  \hfill (11)

$$\rho(\Phi_i^r, \Phi_j^s) = \psi_i^r \psi_j^s,$$  \hfill (12)

$$\rho(\Phi_i^r, \Phi_j^s) = 0.$$  \hfill (13)

where $\rho_{0}$ is the electron density of the ground electronic configuration $\Phi_0$, and $\rho_a = \psi_a^\dagger \psi_a$ ($a = i, r$).

From table 4, the wavefunctions of triplet excited states $T_2@T_2$ and $T_1@T_2$ can be approximately expressed by

$$\Psi_{T_2@T_2} = a \Phi_{LU} + 2 \Phi_{HO} - 2 \Phi_{NLU} \Phi_{NHO},$$  \hfill (14)

$$\Psi_{T_1@T_2} = b \Phi_{NLU} + c \Phi_{HO},$$  \hfill (15)

respectively. Therefore, the overlap density can be written as

$$\rho(\Psi_{T_2@T_2}, \Psi_{T_1@T_2}) = -ab \psi_{NLU}^\dagger \psi_{LU}.$$  \hfill (16)

It should be noted that $\rho(\Phi_{LU}^{NLU}, \Phi_{NHO}^{LU}), \rho(\Phi_{LU}^{NLU}, \Phi_{HO}^{LU})$, and $\rho(\Phi_{NHO}^{LU}, \Phi_{HO}^{LU})$ are vanishing. In other words, the overlap density between $T_2@T_2$ and $T_1@T_2$ are reduced because of the multiconfigurational structure of the TD-DFT wavefunctions. Accordingly, the nonradiative transition from $T_2$ to $T_1$ is suppressed.

Similarly in the $T_3$ adiabatic state, from table 3, the wavefunctions of triplet excited states $T_3@T_3, T_2@T_3, \text{ and } T_1@T_3$ can be approximately expressed by

$$\Psi_{T_3@T_3} = \rho \Phi_{LU}^{LU} + 2 \Phi_{LU}^{HO} - 2 \Phi_{NLU}^{LU} + q \Phi_{NLU}^{LU} - q \Phi_{LU}^{LU},$$  \hfill (17)

$$\Psi_{T_2@T_3} = \rho \Phi_{NLU}^{LU} - p \Phi_{HO}^{LU} - q \Phi_{NLU}^{LU},$$  \hfill (18)

$$\Psi_{T_1@T_3} = -p \Phi_{NLU}^{LU} + r \Phi_{HO}^{LU} + s \Phi_{LU}^{LU}.$$  \hfill (19)

**Figure 8.** Overlap densities between (a) $T_3@T_3$ and $T_2@T_3$, (b) $T_3@T_3$ and $T_1@T_3$, and (c) $T_2@T_2$ and $T_1@T_2$. All the isosurface values are $2 \times 10^{-4}$. 
where \( p \approx 0.4, \ q \approx 0.3, \ r \approx 0.5, \) and \( s \approx 0.2. \) The overlap densities are derived as follows:

\[
\rho(\Psi_{T_3@T_3}, \Psi_{T_2@T_3}) = -p^2 \psi_{LU+2}^* \psi_{NLU} + p(p + q) \psi_{HO-2}^* \psi_{NHO} - q^2 \psi_{LU}^* \psi_{NLU}. \tag{20}
\]

\[
\rho(\Psi_{T_3@T_3}, \Psi_{T_1@T_3}) = \begin{cases} 
q^2 \psi_{LU}^* \psi_{NLU}, & \text{if } p \neq 0, q \neq 0, s = 0, r = 0, \\
q^2 \psi_{LU}^* \psi_{NLU} - q^2 \psi_{LU}^* \psi_{NLU}, & \text{if } p = 0, q \neq 0, s = 0, r = 0, \\
q^2 \psi_{LU}^* \psi_{NLU} + q^2 \psi_{LU}^* \psi_{NLU}, & \text{if } p \neq 0, q = 0, s = 0, r = 0,
\end{cases} \tag{21}
\]

\[
\rho(\Psi_{T_3@T_3}, \Psi_{T_1@T_3}) = -q^2 \psi_{LU}^* \psi_{NLU}, \tag{22}
\]

\[
\rho(\Psi_{T_3@T_3}, \Psi_{T_1@T_3}) = -q^2 \psi_{LU}^* \psi_{NLU} + q^2 \psi_{LU}^* \psi_{NLU} - q^2 \psi_{LU}^* \psi_{NLU}. \tag{23}
\]

The orbital localizations give rise to the reduction of the overlap densities.

5. Conclusion
The pseudodegenerate electronic structure can give rise to the excited state wavefunctions with the multi-configurationality. Offdiagonal VCCs between such excited state wavefunctions can be small because of the reductions of the overlap densities between them. Small VCCs make nonradiative transitions from the higher triplet states to the lower triplet states suppressed. If the energy levels of these excited state, \( T_2 \) and \( T_3 \) in PTZ-BZP, are close to the emitting state, \( S_1 \) in PTZ-BZP, the reverse intersystem crossings from the higher triplet states to the emitting state is possible (fluorescence via higher triplets mechanism). The efficiency of exciton generation in such a system can be high because both singlet and triplet excitons can be utilized under current excitation as is the same in TADF OLED.

For PTZ-BZP, the energy gap between \( S_1 \) and \( T_3 \) is 25 meV, and that between \( S_1 \) and \( T_2 \) is -15 meV. The offdiagonal VCCs between the \( T_3 \) and \( T_2 \) states and those between the \( T_3 \) and \( T_1 \) states are less than \( 3.7 \times 10^{-4} \) a.u., and those between the \( T_2 \) and \( T_1 \) states are less than \( 2 \times 10^{-5} \) a.u. Therefore, the high EQE in PTZ-BZP can be attributed to fluorescence via higher triplet states because of the suppression of the nonradiative transitions from the \( T_3 \) and
$T_2$ states. Since the triplet excitons can be converted to the $S_1$ state via reverse intersystem crossing from these higher triplet states, the efficiency of exciton generation is increased.

To increase EQE, not only the efficiency of exciton generation should be increased, but also the PLQY should be enhanced. From the offdiagonal VCD analysis for the $S_1$ state, the overlap density on the benzothiadiazole moieties should be reduced by some chemical modification to increase the PLQY of PTZ-BZP.

One class of the candidates of the fluorescence via higher triplets mechanism is a set of molecules of X-Y-X type. For PTZ-BZP, BZP is X, and PTZ is Y. Two same moieties of X can yield a pseudodegenerate electronic structure which can give rise to multiconfigurational excited states.

**Acknowledgments**

Numerical calculations were partly performed at the Supercomputer Laboratory of Kyoto University. This study was also supported by a Grant-in-Aid for Scientific Research (C) (15K05607) from the Japan Society for the Promotion of Science (JSPS).

**Appendix**

**Vibronic coupling density operator**

The field operators of an electron are defined by

$$\hat{\psi}(\mathbf{r}_1) := \sum_{b} \psi_b(\mathbf{r}_1) \hat{c}_b, \quad (24)$$

$$\hat{\psi}^\dagger(\mathbf{r}_1) := \sum_{a} \psi^\ast_a(\mathbf{r}_1) \hat{c}_a^\dagger, \quad (25)$$

where $\psi_b(\mathbf{r}_1)$ denotes a molecular orbital, and $\hat{c}_b$ and $\hat{c}_a^\dagger$ are a annihilation and creation operator, respectively.

In second-quantized form, vibronic coupling density operator|18] is written as

$$\hat{\eta}^\alpha(\mathbf{r}_1) := \hat{\psi}^\dagger(\mathbf{r}_1) v^\alpha(\mathbf{r}_1) \hat{\psi}(\mathbf{r}_1) = \sum_{a,b} v_{ab}^\alpha(\mathbf{r}_1) \hat{c}_a^\dagger \hat{c}_b, \quad (26)$$

where potential derivative $v^\alpha(\mathbf{r}_1)$ is defined by

$$v^\alpha(\mathbf{r}_1) := \left( \frac{\partial u(\mathbf{r}_1)}{\partial Q_\alpha} \right)_{\mathbf{R}_0} \text{, with } u(\mathbf{r}_1) = -\sum_{A} \frac{Z_A e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{R}_A|}. \quad (27)$$

Orbital vibronic coupling density (OVCD) $\eta_{ab}^\alpha(\mathbf{r}_1)$ is defined by

$$\eta_{ab}^\alpha(\mathbf{r}_1) := \psi_a^\ast(\mathbf{r}_1) v^\alpha(\mathbf{r}_1) \psi_b(\mathbf{r}_1). \quad (28)$$

Offdiagonal VCC $V_{mn}^\alpha$ can be written by using VCD operator as

$$V_{mn}^\alpha = \langle \Psi_m | \hat{\eta}^\alpha | \Psi_n \rangle = \int \eta_{mn}^\alpha(\mathbf{r}_1) d\mathbf{r}_1. \quad (29)$$

VCD $\eta_{mn}^\alpha(\mathbf{r}_1)$ and OVCD $\eta_{ab}^\alpha(\mathbf{r}_1)$ describe a local picture of a vibronic coupling of mode $\alpha$. 
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