Recent progress on exciplex-emitting OLEDs

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Abstract

The thermally-activated-delayed-fluorescence (TADF) characteristics makes exciplexes being the hot subject in the organic light-emitting diode (OLED) research field. The theoretical limit for the efficiency of the conventional fluorescent OLEDs have been leaped by exploiting the triplet harvesting ability of exciplexes. Exciplexes are easily formed by blending electron donor molecules and electron acceptor molecules, which are generally hole transporting materials and electron transporting materials, respectively, resulting in easy access for employing exciplexes to OLEDs. We introduce the photo-physical characteristics of exciplexes derived from the charge-transfer characteristics and their application to OLEDs as emitters. Single exciplex-emitting OLEDs as well as exciplex emission-based white OLEDs are covered in this review.

1. Introduction

Since C. W. Tang et al. reported organic light-emitting diodes (OLEDs) comprising a hole transport layer and a light emitting layer in 1987 [1], various OLEDs with different structures have been reported. Exploiting emission from exciplexes in OLEDs was also reported in 1994 [2]. Since external quantum efficiencies (EQEs) of exciplex-emitting OLEDs were low, exciplexes were considered as obstacles reducing efficiency in OLEDs. In 2012, however, Goushi et al. and Y.-S Park proposed that exciplexes could transform triplet excited states which do not participate in emission into singlet excited states based on the charge-transfer (CT) characteristics of exciplexes, which could lead to 100% internal quantum efficiency (IQE) without using phosphorescent dyes [3–5]. Goushi et al. demonstrated fluorescent OLEDs with the EQE of 10.0% using a 4,4’,4’’-tris[3-methylphenyl(phenyl)amino]-triphenylamine (m-MT DATA):2,8-bis(diphenylphosphoryl) dibenzo- [b,d] thiophene (PPT) blended layer as an emitting layer, which broke the theoretical EQE limit of conventional fluorescent OLEDs [4]. Y.-S. Park also reported an exciplex-emitting OLED with the emitting layer of the blends of 4,4’,4’’-tris(N-carbazolyl)-triphenylamine (TCTA)/bis-4,6-(3,5-di-3-pyridylphenyl)-2-methylpyrimidine (B3PYMPM). The maximum EQE of the device was 3.1% even though the PLQY of the blends was 36% by virtue of the triplet harvesting of the exciplex [5,6]. Moreover, featureless broad emission spectra of the exciplexes have promoted the introduction of the exciplex emission into white OLEDs (WOLEDs) for good color quality. Studies about exploiting exciplexes in OLEDs are very active now. The purpose of this review is to provide the fundamentals and characteristics of exciplexes and its application to exciplex emission-based OLEDs reported up to now.

2. Excited CT complex

Exciplexes are generated by CT at the excited state between electron donor and electron acceptor molecules, from which the name of exciplex (excited CT complex) originates [7]. The exciplex emission is usually observed in type-II heterojunctions, which consist of a pair of two molecules with the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the donor molecule being higher than those of the acceptor molecule as shown in Figure 1(a). The CT in exciplexes can be considered as the partial CT, and the exciplex wavefunction can be expressed as the mixed state of pure locally ground, locally excited (LE) and CT states as a result of the configuration interaction which is the superposition of the configurations. In this form of wavefunction, the fraction of CT in the exciplex is defined as the square of the...
expansion coefficient for the pure CT state [8,9]. Exciplexes in solution and films were reported to exhibit various fractions of CT dependent on the microscopic environment, librational displacement, and geometries of exciplex-forming pairs [9,10].

A significant feature of exciplexes is their photoluminescence (PL) spectra. As the fraction of CT in the exciplex increases, the PL spectra of exciplexes are redshifted from the PL spectra of the constituent molecules, broad, and featureless without the vibrational progression [9,13]. One example is shown in Figure 1b, where exciplexes are formed between 9,10-dicyanoanthracene (DCA) and various alkylbenzenes such as p-xylene, 1,2,4-trimethylbenzene, 1,2,3,5-tetramethylbenzene, durene, pentamethylbenzene, and hexamethylbenzene in cyclohexane [9]. DCA and the alkylbenzenes are the electron acceptor and electron donors, respectively. The average degrees of CT of each exciplex-forming systems are also given in Figure 1(b). Exciplexes participating in emission have various degrees of CT which are dependent on the microscopic environment and librational displacement. The simulated PL spectra (red curves) of exciplexes are well matched with the experimental ones (black curves). The decrease of the oxidation potentials of the donors corresponding to the increase of the energy levels of the HOMO of the donors leads to the decrease of the energy of the pure CT state. It gives rise to the increase of the average degree of CT of exciplexes, resulting in the reduction of the characteristics from the pure LE state, and the expansion of the characteristics from the pure CT state.

In contrast to the PL spectra of exciplexes, the absorption spectra of exciplexes are usually not observed [14]. However, the existence of sub-band gap intermolecular CT absorption in exciplex-forming systems with very low intensity was reported employing elaborate measurements such as Fourier transform photocurrent spectroscopy (FTPS) and photothermal deflection spectroscopy (PDS) [11,15–22]. These new absorption peaks originate from the direct optical excitation from the ground state to the exciplex state [21]. Recently a much simple method combining UV-Vis-NIR spectrophotometer and ellipsometry measurements has been developed to measure the very weak intermolecular CT absorption with comparable sensitivity to FTPS and PDS [11]. The absorbance of an exciplex-forming mixed film obtained from the reflection/transmission measurement using an UV-Vis-NIR spectrophotometer is analyzed using the transfer matrix method combined with ellipsometry measurement to obtain extinction coefficient for the intermolecular CT state as low as $10^{-4}$. One example is shown in Figure 1c for an exciplex-forming m-MTDATA:2,4,
6-tris[3-(diphenylphosphinyl)phenyl]-1,3,5-triazine (POT2T) mixed film. An extra absorption band from the absorption bands of the pristine films appears in the sub-bandgap region of the consisting molecules with the extinction coefficients below 10\(^{-3}\), which corresponds to the exciplex absorption band. The low absorption coefficient of the singlet exciplex state is attributed to the CT characteristics of exciplexes which is called the overlap forbiddeness [7].

The transition rate constants in exciplex-forming systems are also influenced by the degree of CT of exciplexes, \(f_{CT}\) [9,12,13,23–39]. The fluorescence rate constants \((k_f)\), nonradiative rate constants \((k_{nr})\), and intersystem crossing (ISC) rate constants \((k_{isc})\) of the singlet exciplex states between 2,6,9,10-tetracyanoanthracene (TCA) and DCA as electron acceptors and various alkylbenzenes as electron donors in various solvents are plotted as a function of the average emission energy of singlet exciplex states in Figure 1(d) [12]. \(k_f\) of the singlet exciplex state decreases with \(f_{CT}\) due to the decrease of the LE character in the singlet exciplex state. \(k_{nr}\) of them decreases with \(f_{CT}\) at first due to the decrease of the LE character in the singlet exciplex state, but increases with \(f_{CT}\) when \(f_{CT}\) is larger than 0.7 due to the decrease of the energy difference between the singlet exciplex state and the ground state. \(k_{isc}\) of them increases with \(f_{CT}\) due to the decrease of the energy difference between the singlet exciplex state and the triplet LE state. In the exciplex-forming systems, the triplet LE state energy was the lowest triplet state energy of DCA and TCA, which is \(13,100 \text{ cm}^{-1}\) [31].

The ISC and reverse intersystem crossing (RISC) are the spin-forbidden transition [7]. Transition probability of them is zero when 0th order approximation. However, state mixing could explain the nonzero probability for the transitions [7]. There are two significant mechanisms for mixing singlet and triplet states of exciplexes. One is the spin-orbit coupling, and the other is the hyperfine interaction. The spin-orbit coupling is caused by the magnetic torque generated by the electron orbital motion which could change the electron spin [7]. The matrix elements of the spin-orbit coupling of the pure CT state are zero based on the one-electron approximation [40].

Thus, the hyperfine interaction plays a major role for the ISC and RISC of the pure CT state \((f_{CT} = 1)\) instead of the spin-orbit coupling [31,41]. The hyperfine interaction is induced by the magnetic torques due to nuclear spin of molecules [7]. It becomes negligible compared to the spin-orbit coupling if the electronic coupling between the singlet and triplet states is not weak, achieved by the configuration interaction of pure CT states with other LE states as well as the small singlet-triplet energy splitting [7,31,42]. In the case of the ISC from the highly ionic singlet exciplex state to the highly ionic triplet exciplex state, the matrix elements of the spin-orbit coupling for the ISC are small because of the high degree of CT of two states. Then, the ISC from the highly ionic singlet exciplex state to the highly neutral triplet exciplex state could be faster than the ISC from the highly ionic singlet exciplex state to the highly ionic triplet exciplex state [40]. It implies that the transition from the highly ionic singlet exciplex state to the highly neutral triplet exciplex state would be governed by the direct transition from the highly ionic singlet exciplex state to the highly neutral triplet exciplex state rather than the transition via the highly ionic triplet exciplex state [31,40]. It indicates that ISC and RISC could be accelerated when energy levels of the highly ionic singlet exciplex state and the highly neutral triplet exciplex state are similar [43].

3. Thermally activated delayed fluorescence

Thermally activated delayed fluorescence (TADF) of exciplexes have become the center of attention since it was reported in the OLED research field. In the past, OLEDs employing pure organic molecules without heavy atoms had the limit of 25% for generating singlet excitons from polarons. Considering that only the singlet exciton is the radiative species in room temperature without heavy atoms, it had served as the obstacles for achieving highly efficient OLEDs over the IQE of 25%. Beginning with the report of the OLEDs exploiting the TADF of exciplexes, however, the theoretical limit for generating singlet excitons from polarons reaches 100% without heavy atoms. The TADF of exciplexes has been the core value for the third generation OLEDs along with intra-molecular CT molecules.

The small singlet-triplet energy splitting of exciplexes causes the TADF. In other words, the transition from the triplet exciplex state to the singlet exciplex state plays a major role in the TADF. The singlet exciplex state undergoes transitions to the ground state by the radiative (fluorescent) and nonradiative ways (internal conversion) as well as the transition to the triplet exciplex state by the nonradiative way (ISC). The triplet exciplex state also undergoes the transitions to the singlet exciplex state by the nonradiative way (RISC) and to the ground state with the radiative (phosphorescent) and the nonradiative ways. Conventional fluorescent molecules have very small RISC rate constant at room temperature due to large singlet-triplet energy splitting, so the lowest triplet excited state has little transition probability to the lowest singlet excited state. On the other hand, exciplexes could have large transition probability for the RISC from the triplet excited state to the singlet excited state at room temperature. It is attributed to small singlet–triplet energy
splitting of exciplexes, resulting in strong delayed fluorescence originated from efficient RISC process, followed by the fluorescence process. This is called TADF [3,44,45]. Efficient RISC process could be achieved when energy levels of the highly ionic singlet exciplex state and the highly neutral triplet exciplex state are similar [43].

The state energy diagram of the exciplex-forming system which is typically employed in exciplex-emitting OLEDs is shown in Figure 2(a). The basis states of the exciplex-forming system are denoted as $S_{LE}$, $S_{CT}$, $T_{LE}$, and $T_{CT}$ which are the lowest singlet LE state, the lowest singlet CT state, the lowest triplet LE state, and the lowest triplet CT state, respectively, based on the three-state mixing model for each singlet and triplet states [35]. $S_{CT}$ and $T_{CT}$ which are generated in the exciplex-forming system induce the effective state mixing between the states with the same spin multiplicity, resulting in $S_1$, $S_2$, $T_1$, and $T_2$ states, which are the lowest singlet excited state, the second lowest singlet excited state, the lowest triplet excited state, and the second lowest triplet excited state in exciplex-forming system. They have the both the CT character and the LE character by virtue of the state mixing. The mixing coefficients decide the degrees of CT of the mixed states [9,35]. Exciplexes showing effective TADF characteristics usually have $T_{LE}$ and $T_{CT}$ with the similar energy levels, inducing moderately neutral triplet exciplex state ($T_1$) [43]. The moderately neutral triplet exciplex state exhibits considerable LE character, and effective ISC and RISC could occur by virtue of the state mixing between the singlet and triplet states when their energy levels are close [3,7,31,40,43].

Concentrations of the lowest singlet and triplet states showing TADF characteristics follow the below equations when photoexcitation is applied as a delta function at $t = 0$ [3].

$$\frac{d[S_1]}{dt} = -(k^S_g + k_{isc})[S_1] + k_{risc}[T_1]$$

$$\frac{d[T_1]}{dt} = -(k^T_g + k_{risc})[T_1] + k_{isc}[S_1]$$

where $[S_1]$ and $[T_1]$ are the concentrations of the lowest singlet and triplet excited states, respectively, $k^S_g$, $k^T_g$, $k_{isc}$, $k_{risc}$ are the transition rate constants from the singlet state to the ground state and that from the triplet state to the ground state, that from the singlet state to the triplet state, and that from the triplet state to the singlet state, respectively, which are depicted in Figure 2(a). The solution for the differential equations are the below equations when the initial condition is $[T_1] = 0$ for the case of photoexcitation at $t = 0$ as a delta function.

$$[S_1] = C_p \exp(-k_p t) + C_d \exp(-k_d t)$$

$$[T_1] = -C_T \exp(-k_p t) + C_T \exp(-k_d t)$$

where $k_p$ and $k_d$ are the prompt and delayed fluorescence rate constants, respectively, $C_p$ and $C_d$ are the prompt and delayed pre-exponential factors for the singlet states, respectively, and $C_T$ is the pre-exponential factor for the triplet state [3,46–48].

One example following the equations is depicted in Figure 2(b). The population of the singlet state is usually dominant in the prompt time region, and that of the triplet state is usually dominant in the delayed time region because the lifetime of the singlet states is usually shorter than that of the triplet states. Transient PL intensities of exciplexes follow the black curve in Figure 2(b) because the PL intensity is linearly proportional to $[S_1]$. The key transition which could make TADF characteristics is the RISC. As the ISC and RISC quantum yield increases, the delayed part of the transient PL profiles becomes dominant. The high RISC quantum yield indicates the efficient harvesting of the triplet excited states to the singlet excited states (emissive states).

The quantum-mechanical equation for $k_{risc}$ could be transformed into the Arrhenius equation if the vibrational states are treated classically, which is Equation (5) [3,47,49–51].

$$k_{risc} = A \exp \left( -\frac{\Delta E_{ST}}{k_B T} \right)$$

Figure 2. (a) State energy diagram of the exciplex-forming system. (b) Typical semilogarithmic plots for concentration profiles of singlet (black) and triplet (red) excited states exhibiting TADF characteristics.
where $A$ is the pre-exponential factor, $\Delta E_{ST}$ is the singlet-triplet energy splitting, $k_B$ is the Boltzmann constant, and $T$ is the temperature. The thermal distribution corresponds to the Boltzmann distribution, and the thermal equilibration rate of the vibrational states is much faster than the radiationless quantum transition rate between the singlet and triplet states for Equation (5). $\Delta E_{ST}$ of the m-MTDATA: 2-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (t-Bu-PBD) exciplex in the 50 mol% m-MTDATA:t-Bu-PBD blended film was obtained from Equation (5), which is about 50 meV [3]. Considering $k_B T \approx 25$ meV at room temperature, $\Delta E_{ST} = 50$ meV is small enough to help $k_{risc}$ being large contribution to exciplex fluorescence. The free energy change between the single singlet state and the single triplet state could be obtained from the relation between the free energy change and the equilibrium constant of the reaction as given in Equation (6) [46,52].

$$\Delta G_{ST} = RT \ln \frac{k_{isc}}{3k_{risc}} \quad (6)$$

where $\Delta G_{ST}$ is equal to the free energy change between singlet and triplet states and a factor of 3 is for the number of the degeneracy of the triplet states. Using Equation (6), 26 meV was obtained for $\Delta G_{ST}$ of the 9,9′,9″-triphenyl-9H,9′H,9″H-3,3′,6′,3″′-tercarbazole (Tris-PCz): 3′,3″′,3‴′′′-(1,3,5-triazine-2,4,6-triyl)tris([1,1′-biphenyl]-3-carbonitrile)) (CN-T2T) exciplex in the Tris-PCz:CN-T2T blended film [46].

The PLQY of the exciplexes is not just the portion of the radiative decay rate constant in the decay process of the singlet excited state when TADF takes place. The PLQY in exciplexes is the sum between the PLQY from prompt fluorescence and that from delayed fluorescence. The prompt PLQY ($\Phi_{p}$) is the portion of the radiative decay rate constant in the decay process of the singlet excited state which is $k_{f}/(k_{f} + k_{nr} + k_{isc})$. The delayed PLQY ($\Phi_{d}$) could be written as the below equation [3].

$$\Phi_{d} = \Phi_{p} \sum_{k=1}^{\infty} (\Phi_{isc} \Phi_{risc})^{k} \quad (7)$$

Where $\Phi_{isc}$ and $\Phi_{risc}$ are the ISC and RISC quantum yields, respectively. The ISC and RISC quantum yields could be expressed by $k_{isc}/(k_{f} + k_{nr} + k_{isc})$ and $k_{risc}/(k_{nr} + k_{risc})$ where $k_{nr}$ is the nonradiative decay rate constant from the triplet state to the ground state, respectively. Then, the PLQY of the exciplexes could be expressed by the below equation if phosphorescence from exciplexes is negligible compared to fluorescence.

$$\text{PLQY} = \frac{k_{f}}{k_{f} + k_{nr} + k_{isc}(1 - \Phi_{risc})} \quad (8)$$

The 100% PLQY could be achieved by two ways according to Equation (8). The one way is when $k_{f} \gg k_{nr}, k_{isc}$. In that case, the delayed fluorescence becomes negligible in the PL process because the transition from the singlet excited states to the triplet excited states becomes negligible. The other way is when $k_{f} \gg k_{nr}$ and $\Phi_{risc} = 1$. In this situation, triplet loss becomes zero even though the transition from the singlet excited states to the triplet excited states is considerable.

### 4. Exciplex-emitting OLEDs

OLEDs are optoelectronic devices using the electroluminescence (EL). The first step of the EL is the encounter of a positive polaron (free hole) and a negative polaron (free electron). Free polarons have the same probability of the up-spin and the down-spin. The initial formation ratio of singlet states and triplet states by the encounter of a positive polaron and a negative polaron would be 1:3 consisting of S and T₊, T₀, and T₋ states. Conventional fluorescent emitters with the large singlet-triplet energy splitting cannot exploit triplet excitons as photons in anyway because the nonradiative transition rate from T₁ to S₁ is much smaller than that from T₁ to S₀. As the singlet-triplet energy splitting increases, the RISC rate usually decreases. As the energy gap between T₁ and S₀ decreases, the nonradiative transition rate from T₁ to S₀ usually increases [53]. On the other hand, exciplexes with the small singlet-triplet energy splitting, resulting in the increase of $k_{isc}$ and $k_{risc}$. The large $k_{risc}$ could enhance the transformation ratio of the triplet exciplex state to the singlet exciplex state, resulting in high efficiency of the OLEDs using exciplexes as emitters.

The triplet harvesting ability of exciplexes makes EQEs of OLEDs employing exciplexes increase compared to conventional fluorescent OLEDs. The equation for EQE of OLEDs employing exciplexes as emitting species can be written as Equation (9) if the intensity of phosphorescence is negligible [3].

$$\text{EQE} = \eta_{OC} \gamma (0.25 + 0.75 \Phi_{risc}) \text{PLQYP} \quad (9)$$

where $\eta_{OC}$ is the light-out coupling efficiency which is considered to be 25–30% without any light-out coupling ways when the emitting transition dipole moment vectors are randomly distributed, $\gamma$ is the recombination efficiency of electrons and holes in OLEDs, and PLQYP is the PL quantum yield of the exciplexes in microcavity structures of OLEDs. PLQYP of the exciplexes is the same with Equation (8) but $k_{f}$ changes into $Fk_{f}$ where $F$ is the Purcell factor. The EQE of OLEDs increases when $\Phi_{risc}$ or PLQYP of exciplexes increases. The increase of $\Phi_{risc}$ helps to improve the triplet harvesting ability, and
the increase of PLQYP helps to improve the transition ability of the energy of singlet excited species to photons. The high $\Phi_{\text{risc}}$ and PLQYP of the exciplex systems are necessary for highly efficient exciplex-emitting OLEDs. The maximum EQE of OLEDs using exciplexes as emitters can be achieved when $\Phi_{\text{risc}} = 1$. $\Phi_{\text{risc}} = 1$ leads to the PLQYP to be $F_k / (F_k + k_{\text{nr}})$, and PLQYP $= 1$ if $F_k \gg k_{\text{nr}}$. Then, the maximum EQE becomes $\eta_{\text{OC}}$. If the singlet-triplet energy splitting is large or $T_1$ state is the highly ionic exciplex state, they would have small $\Phi_{\text{risc}}$. When $\Phi_{\text{risc}} = 0$, Equation (9) becomes the case for OLEDs using conventional fluorescent emitters.

### 4.1. Emitting structure composed of a donor and an acceptor

In 2003, L. C. Palilis et al. reported efficient exciplex emission between $N,N'$-diphenyl-$N,N'$-(2-naphthyl)-(1,1'-phenyl)-4,4'-diamine (NPB) and 2,5-di-(3-biphenyl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene (PPSPP) with the PLQY of 62% in the blended film even though exciplex was thought to be inefficient emitting species because of the low transition dipole moment [54]. They fabricated the OLEDs with the organic trilayer composed of NPB, PPSPP, and 2,5-bis-(2',2''-bipyridin-6-yl)-1,1-dimethyl-3,4-diphenylsilacyclopentadiene (PyPySPyPy). The EL emission was originated from the interface exciplex between NPB and PPSPP with the EL peak of 495 nm and the EQE of 3.4%. The EQE was lower than theoretical limit of the conventional fluorescent OLEDs because the TADF characteristics of the exciplexes could not employed due to the low $T_1$ state of NPB, resulting in the large singlet-triplet energy splitting.

In 2012, K. Goushi et al. reported an OLED with the higher EQE than the theoretical EQE limit of the conventional fluorescent OLEDs [3]. The emitting layer of the OLED is a blended layer of m-MTDATA/t-Bu-PBD of which structures are shown in Figure 3(a). The redshifted featureless emission of the blended film implies that they form the exciplex as shown in Figure 3(b). Even though the PLQY of the blended film was 20%, the EQE of the OLED was 2%, of which emitting layer is the blended layer of m-MTDATA and t-Bu-PBD as shown in Figure 3(c). Considering that the theoretical limit for the EQE of conventional fluorescent OLEDs with the PLQY of 20% of the emitting layer is around 1.0 $\sim$ 1.5%, the triplet harvesting process occurs in the OLED, and its mechanism is TADF. The transient PL and EL both followed the two-exponential decay form consisting of prompt and delayed decays with similar decay constants as shown in Figure 3(d). The singlet-triplet energy splitting of the exciplex was 50 meV obtained by the analysis of the transient PL profiles at various temperatures, which is close to the thermal energy at the

![Figure 3](image-url)
Figure 4. (a) Molecular structures of TCTA and B3PYMPM; (b) PL spectra of the TCTA, B3PYMPM, and TCTA:B3PYMPM films; (c) Total, prompt, and delayed PLQY of the TCTA:B3PYMPM film as a function of temperature; (d) EQE and applied voltage at the current density of 0.1 mA/cm² of the exciplex-emitting OLED at various temperature (ref. [6]).

room temperature (∼ 25 meV). Such small singlet-triplet energy splitting of the exciplex promotes the TADF process by virtue of large RISC rate constant. They also reported an OLED with the EQE of 5.4% employing the blended layer between m-MTDATA and tris-[3-(3-pyridyl)mesityl]borane (3TPYMB) with the PLQY of 26% [3]. Y.-S. Park et al. also reported an exciplex-emitting OLED with the emitting layer of the blends of TCTA/B3PYMPM whose structure are shown in Figure 4(a) [5,6]. They form the exciplex considering that the blended film emits a different emission band different from molecule emissions as shown in Figure 4(b). The PLQY of the blends was 36%, and the maximum EQE of the device was 3.1%. It indicates that the triplet harvesting of the exciplex operates in the device. They also reported that the EQE of the device increases as the temperature decreases due to the decrease of the nonradiative decay to the ground state with temperature in the exciplex-forming system leading to the increase of the PLQY of the blends as shown in Figure 4(c,d). The PLQY of the blends reaches 99% at 35 K and the EQE of the device reaches 10% at 195 K at which the PLQY of the blends was 87% when the current density was 0.1 mA/cm². Their reports open up possibility that the increase of EQEs using exciplexes could be a key for efficient fluorescent OLEDs with the EQE over 30% like phosphorescent OLEDs.

Exciplex-emitting OLEDs have been actively studied since their reports. Many of them employed exciplexes between hole transporting materials and electron transporting materials [46,49,55–81]. An iridium-containing phosphorescent material, however, was also exploited for the exciplex-emitting OLED. V. Cherpak et al. reported an OLED exhibiting exciplex emission between 4,4′,4″-tris[3-methylphenyl(phenyl)amino] triphenylamine and tri(9-hexylcarbazol-3-yl)amine (THCA) and iridium(III) bis[(4,6-difluorophenyl)pyridinato-N,C2′]picolinate (FIrpic) [78]. The PL peaks of THCA and FIrpic were 470 nm, and that of the exciplex was 570 nm. The device structure was ITO/CuI/THCA/FIrpic/3,6-di(9-carbazolyl)-9-(2ethylhexyl)carbazole (TCz1)/Ca/Al, and the EQE of the device was 5%. The singlet-triplet energy splittings were 35, 3.8, and 7.5 meV which were calculated by the time-dependent density functional theory (DFT) approximation at the B3LYP/6-31G(d)/Lanl2DZ method at three different geometries of THCA/FIrpic complexes. The small singlet-triplet energy splitting indicates that the RISC process could be effectively occurred at room temperature. The phosphorescence from the triplet exciplex state by virtue of the heavy atom of FIrpic as well as the TADF would induce the broad PL and EL spectra.

K.-H. Kim et al. demonstrated the exciplex-emitting OLED with the EQE of 25.2% at 150 K. The emitting layer of the device was blends of TCTA/4,6-bis[3,5(dipryrid-4-yl)phenyl]-2-methylpyrimidine (B4PYMPM) of which the PL peak wavelength and singlet-triplet energy
splitting were 509 nm and 8.5 meV, respectively [49]. The EQE and PLQY were 11% and 60%, respectively, at room temperature. As the temperature decreases, the EQE and PLQY increase, leading to the EQE of 25.2% and the PLQY of 100% at 150 K. The calculated out-coupling efficiency of the device at 150 K was 26.6%, implying that the almost all triplet excited states in the device were harvested at 150 K. The highest EQE of the reported exciplex-emitting OLEDs at room temperature with the emitting layer of the donor-acceptor blended layer is 20.9%, which was reported in 2019 [73]. The emitting layer of the device was the blends of 4,4′-(diphenylsilanediyl)bis(N,N-diphenylaniline) (TSBPA)/PO-T2T. Their structures are shown in Figure 5(a) and the EL spectra peak was at 528 nm. The redshifted featureless emission spectrum and delayed emission of their blends indicate that they form the exciplex as shown in Figure 5(b,c). The structure of the device was ITO/NPB/TSBPA/TSBPA:PO-T2T/PO-T2T/LiF/Al of which EQE curve versus current density is shown in Figure 5(d). The PLQY of the exciplex-forming blends was 100%, and the high EL efficiency can be achieved. They also reported blue exciplex-emitting OLED with the EL spectra peaking at 480 nm of which the Commission Internationale de L’Eclairage (CIE) coordinates was (0.16, 0.28). The emitting layer was the blends of 1,3-bis(N-carbazolyl)benzene (mCP)/PO-T2T of which the PLQY was 55% [73]. The maximum EQE was 16% as shown in Figure 5(d). It is the same efficiency with the blue exciplex-emitting OLED with the emitting layer of CN-Cz2:PO-T2T mixtures which was reported in 2018 [72].

4.2. Emitting structure composed of a donor, an acceptor, and a functional molecule

Generally, exciplexes formed at bilayers between a donor layer and an acceptor layer or donor-acceptor blends have been employed for exciplex-emitting OLEDs. There are reports that a trilayer consisting of a donor layer, a spacer layer, and an acceptor layer was employed for emitting structure of the exciplex-emitting OLEDs [82,83]. H. Nakanotani et al. reported the exciplex-emitting OLED with an emitting structure of the trilayer consisting of a m-MTDATA layer, a 3,3-di(9H-carbazol-9-yl)biphenyl (mCBP) layer, and a 2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine (T2T). m-MTDATA, mCBP, and T2T layers act as a donor layer, a spacer layer, and an acceptor layer, respectively [82]. m-MTDATA and T2T form exciplexes exhibiting fluorescent luminescence with a peak wavelength of ~550 nm in the trilayer structure. The device structure employing the trilayer structure was ITO/m-MTDATA/mCBP/T2T/tris(8-hydroxyquinolino) aluminum (Alq3)/LiF/Al, and the layer thickness of mCBP was varied from 0 to 15 nm. The EL spectra of the devices show exciplex emission only when the thickness of the spacer layer is under 3 nm, and molecule emissions only when the thickness of the spacer layer is over 10 nm. The maximum EQE of the devices was 2.5% when the spacer thickness is 5 nm, which is higher than the EQE of the OLEDs employing exciplexes formed at the bilayer between a donor layer and an acceptor layer or donor-acceptor blends which are 0.5% and 0.9%, respectively. The reduction of the nonradiative decay of the triplet state to the ground state of the exciplex in trilayer
structure would help to increase the efficiency of the device.

Exciplex-emitting OLEDs with donor-acceptor-diluter blends were also reported by M. Colella et al. different from typical exciplex-emitting OLEDs with donor-acceptor blends [84]. They employed TSBPA and PO-T2T as the electron donor and acceptor, respectively. The diluter was 1,3-bis(triphenylsilyl)benzene (UGH-3) whose structure is shown in Figure 6(a). As the concentration of the diluter increases, the PL spectra of the exciplex in the donor-acceptor-diluter blends show blue-shift because of the increase of the donor-acceptor separation as shown in Figure 6(b), and the PL intensity from the molecules increases. The molecule/exciplex ratio of the PL intensity was larger than 0.1 when the concentration of UGH-3 was larger than 70 vol% due to the increase of the donor-acceptor separation. The PLQY of the donor-acceptor blends was 58%, and the maximum PLQY of the donor-acceptor-diluter blends was 80% when the concentration of UGH-3 was 50 vol% by virtue of the decrease of concentration quenching of the exciplex as shown in Figure 6(c). The increase of the PLQY of the exciplex in the blends leads to the increase of the EQE of the OLED exploiting donor-acceptor-diluter blends. The maximum EQE of the devices was 19.2% when the donor-acceptor-diluter blends with 50 vol% UGH-3 was employed as the emitting layer of the device as shown in Figure 6(d), which is higher value than 14.8% which is the EQE of the device with emitting layer of the donor-acceptor blends.

4.3. TTA-dominant exciplex-emitting OLEDs

TADF is always not the dominant way for triplet harvesting process in OLEDs employing exciplexes as emitting species [6,50,85,86]. The triplet-triplet annihilation (TTA) was proposed as another mechanism for triplet harvesting process [85,86]. The encounter of two T1’s can generate S1 and S0 in TTA process, resulting in the theoretical maximum IQE of TTA OLEDs of 62.5%. V. Jankus et al. reported the exciplex-emitting OLED with the emitting layer of the blends of NPB/1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi) whose structures are shown in Figure 7(a) [86]. The PLQY of the blends was 28%, and the EQE of the device was 2.7% exceeding the theoretical EQE limit of conventional fluorescent OLEDs as shown in Figure 7(b). They, however, proposed that the triplet harvesting process in the device arose from the TTA process of the NPB T1 states. The S1 and T1 energy of NPB were 3.1 and 2.38 eV, respectively. When TTA process is dominant, the transient PL profiles of delayed emission shows power law decay whose slope changes from $-1$ to $-2$. When energetically randomly

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**Figure 6.** (a) Molecular structure of UGH-3; (b) PL spectra of the TSBPA:PO-T2T:UGH-3 films with various volume percentages of UGH-3; (c) PLQY of the TSBPA:PO-T2T:UGH-3 films and TSBPA:PO-T2T:DPEPO films with different volume percents of UGH-3 and DPEPO, respectively, in air and nitrogen atmospheres; (d) EQE as a function of luminance for the exciplex-emitting OLEDs (ref. [84]).
generated triplet states relax towards the tail of the density states resulting in the time-dependent rate constant for the TTA process, the slope of the power law decay is $-1$. After the energetic relaxation of the triplet states, the rate constant for the TTA process becomes time-independent leading to the power law decay of delayed emission with slope of $-2$ [86]. The delayed emission of the neat NPB film follows the power law decay whose slope changes from $-1$ to $-2$, and the delayed PL emission of the blends and EL emission also follow the power law decay as shown in Figure 7(c). It implies that the TTA process takes place for the NPB T$_1$ state in the NPB:TPBi blends. The TTA process is the bimolecular reaction so that the intensity of the delayed emission arising from the TTA is linearly proportional to the square of concentration of the T$_1$ state compared to the TADF process of which delayed emission intensity is linearly proportional to the concentration of the T$_1$ state [50,86]. Therefore, the delayed emission intensity follows a quadratic dependence on the excitation intensity if the TTA process is dominant. The delayed emission intensity of the blends follows the quadratic dependence on the excitation intensity as shown in Figure 7(d). It implies that the TTA process is dominant for the delayed emission of the NPB:TPBi blends and the triplet harvesting process. The characteristics of the OLEDs described in section 4 are summarized in Table 1.

![Figure 7](image)

**Figure 7.** (a) Molecular structures of NPB and TPBi; (b) EQE as a function of applied voltage for the exciplex-emitting OLED; (c) Transient PL profiles of the NPB (red) and NPB:TPBi (black) films and transient EL profile (green) of the exciplex-emitting OLED; (d) Delayed PL emission intensity (circle) of the NPB:TPBi film (ref. [86]).

| Emitting Structure | PLQY (%) | Maximum EQE (%) | EL peak (nm) | Year | Ref. |
|--------------------|----------|-----------------|-------------|------|------|
| NPB/PPSPP         | 62$^a$   | 3.4             | 495         | 2003 | [54] |
| m-MTDATA:t-Bu-PBD (m.r 1:1) | 20 | 2 | – | 2012 | [3] |
| m-MTDATA:3TPYMB (m.r 1:1) | 26 | 5.4 | 543 | 2012 | [3] |
| NPB:TPBi (1:1)    | 28       | 2.7             | 450         | 2013 | [86] |
| TCTA:B3PYMPM (m.r 1:1) | 36 | 3.1 | 506 | 2013 | [6] |
| THCA/FIrpic       | –        | 5               | 572         | 2015 | [78] |
| m-MTDATA:T2T      | 5        | 0.9             | –           | 2016 | [82] |
| m-MTDATA/T2T      | 5$^a$    | 0.5             | 592         | 2016 | [82] |
| m-MTDATA/mCBP (5 nm)/T2T | 5$^a$ | 2.5 | 563 | 2016 | [82] |
| TCTA:B4PYMPM (m.r 1:1) | 60 | 11.0 | 530 | 2016 | [49] |
| CN-Cz2:PO-T2T (w.r 1:1) | 55 | 16 | 474 | 2018 | [72] |
| TSBA:PO-T2T (1:1) | 58       | 14.8            | 535         | 2019 | [84] |
| 50 vol% UGH-3:TSBA:PO-T2T (1:1) | 80 | 19.2 | 526 | 2019 | [84] |
| mCP:PO-T2T (1:1)  | 55       | 16              | 480         | 2019 | [73] |
| TSBA:PO-T2T (1:1) | 100      | 20.9            | 528         | 2019 | [73] |

$^a$ Measured values for blendsof donor/acceptor.
$^b$ Measured values at 150 K.

| Emitting Structure | PLQY (%) | Maximum EQE (%) | EL peak (nm) | Year | Ref. |
|--------------------|----------|-----------------|-------------|------|------|
| NPB/PPSPP         | 62$^a$   | 3.4             | 495         | 2003 | [54] |
| m-MTDATA:t-Bu-PBD (m.r 1:1) | 20 | 2 | – | 2012 | [3] |
| m-MTDATA:3TPYMB (m.r 1:1) | 26 | 5.4 | 543 | 2012 | [3] |
| NPB:TPBi (1:1)    | 28       | 2.7             | 450         | 2013 | [86] |
| m-MTDATA:T2T      | 5        | 0.9             | –           | 2016 | [82] |
| m-MTDATA/T2T      | 5$^a$    | 0.5             | 592         | 2016 | [82] |
| m-MTDATA/mCBP (5 nm)/T2T | 5$^a$ | 2.5 | 563 | 2016 | [82] |
| TCTA:B4PYMPM (m.r 1:1) | 60 | 11.0 | 530 | 2016 | [49] |
| CN-Cz2:PO-T2T (w.r 1:1) | 55 | 16 | 474 | 2018 | [72] |
| TSBA:PO-T2T (1:1) | 58       | 14.8            | 535         | 2019 | [84] |
| 50 vol% UGH-3:TSBA:PO-T2T (1:1) | 80 | 19.2 | 526 | 2019 | [84] |
| mCP:PO-T2T (1:1)  | 55       | 16              | 480         | 2019 | [73] |
| TSBA:PO-T2T (1:1) | 100      | 20.9            | 528         | 2019 | [73] |

5. Exciplex emission-based WOLEDs

Exciplex emission has been employed for WOLEDs as the emission of conventional fluorescence and phosphorescence does. At the early stage, the broad featureless emission bands of exciplexes was considered as the only advantage for WOLEDs with good color quality.
As exciplexes were reported to have triplet harvesting ability, however, exciplexes have become a more important candidate for emitters of WOLEDs with good color quality and efficiency. The emission types of WOLEDs employing exciplex emission are various. Various combinations among exciplex emission, molecule emission, dopant emission, and excimer emission were employed for exciplex emission-based WOLEDs.

### 5.1. Emitting layer of a single donor-acceptor blend

There are various types of structures for WOLEDs. The simple one is a single donor-acceptor blend employed as the emitting layer for WOLEDs [87-90]. M. Mazzeo et al. reported a WOLED with the emitting layer of blends of N,N′-bis(3-methyl-phenyl)-N,N′-diphenylbenzidine (TPD) and 2,5-bis(trimethylsilyl thiophene)-1,1-dioxide (STO) [87]. Exciplex formation between TPD and STO was incomplete in the blends, and white EL emission was comprised of blue emission from the TPD molecule and orange emission from the TPD:STO exciplex. The CIE coordinates of EL spectrum were \( x = 0.34, y = 0.38 \), which are close to the equal-energy white point. The single emitting layer of the donor-acceptor blends does not always emit the combination of a molecule emission band and an exciplex emission band. J. Kalinowski et al. demonstrated white EL emission comprised of exciplex emission, molecule emission, and excimer emission as shown in Figure 8(a) [89]. The three different emissions came from the blends of m-MTDATA/platinum [methyl-3,5-di-(2-pyridyl) benzoate] chloride (PtL₂Cl). m-MTDATA and PtL₂Cl form the exciplex. However, the exciplex formation was incomplete, and the phosphorescent molecule and excimer emission from PtL₂Cl were also implemented in the WOLED whose structure is shown in Figure 8(b) along with the molecular structures. The CIE coordinates were \( x = 0.46, y = 0.45 \) and the color rendering index of CRI was 90 which was a high value given that CRI of 100 is for ideal white light. The maximum EQE was 6.5% as shown in Figure 8(c). The broad featureless emissions from the excimer and exciplex as well as the emissions from three different sources with a different peak wavelength contribute to the good color quality of the device.

### 5.2. Emitting structure of multiple donor-acceptor blends

The multiple exciplex-forming blended layers were employed for WOLEDs [81,91-94]. The WOLED with four different exciplex emission bands was demonstrated employing two different donor-acceptor blends [91]. The four different exciplexes were TPD:4,7-diphenyl-1,10-phenanthroline (Bphen), m-MTDATA:Bphen, TPD:tris (dibenzoyl methane)-aluminum (Al(DBM)₃), and m-MTDATA:Al(DBM)₃ exciplexes with blue, green, orange, and red exciplex emission bands, respectively. The emitting structure of the device was the bilayer between

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**Figure 8.** (a) EL spectrum of the WOLED at the applied voltage of 22 V and PL spectra of TPD:polycarbonate (PC) (75:25), PtL₂Cl:PC (5:95), m-MTDATA:PtL₂Cl (20:1), and m-MTDATA:PtL₂Cl (1:1) films; (b) Molecular orbital energy diagram of the WOLED and the structures of molecules employed in the WOLED; (c) Current efficiency (square) and EQE (circle) as a function of current density for the WOLED (ref. [89]).
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the m-MTDATA:Al(DBM)3 blends and the TPD:Bphen blends. The molecule emission was not detected in the EL spectrum. By virtue of wide four exciplex bands with different color, the CIE coordinates of (0.33, 0.35) and the CRI of 94.1 were obtained at the applied voltage of 10 V. The CRI drops as the applied voltage increases from 10 V because the portion of blue emission increases. The WOLED with two different exciplex-forming blends split with a 3-nm thickness spacer of bis(2-(diphenylphosphino)phenyl)ether oxide (DPEPO) was also reported [92]. The device structure was ITO/MoO3/di-[4-(N,N-ditolyl-amino)-phenyl]cyclohexane (TAPC)/DPEPO/TAPC:PO-T2T/DPEPO/mCP:PO-T2T/DPEPO/PO-T2T/LiF/Al. The EL spectrum of the device was comprised of blue emission from the blends of mCP/PO-T2T and orange emission from the blends of TAPC/PO-T2T whose PL spectra are shown in Figure 9(a). The CIE coordinates, CRI, and maximum EQE were (0.31, 0.37), 84, and 7.92%, respectively as shown in Figure 9(b,c). The transport, recombination, and confinement of polarons and excitons in the WOLED could be balanced by the insertion of the thin spacers, resulting in similar EL spectra with various applied voltages as shown in Figure 9(c). Tandem all-exciplex-based WOLEDs were also reported [81,93]. W.-Y. Hung et al. introduced Liq/Al/MoO3 structure as a charge generation layer of the tandem all-exciplex based WOLED [93]. Two emitting layers were an mCP:PO-T2T blends and a 9,9-di[4-(di-p-tolyl)aminophenyl]fluorine (DTAF):PO-T2T blends, which emit blue and yellow exciplex emission bands, respectively. The CIE coordinates and CRI were (0.28, 0.34) and 70.6 at 11,400 cd/m², respectively. The maximum EQE of 11.6% was obtained in the tandem all-exciplex-based WOLED.

5.3. Multilayer emitting structures

Multilayer structures of donors and acceptors were also exploited for WOLEDs [14,90,95–99]. A. P. Kulkarni et al. employed the bilayer between a blends of 25 wt% polystyrene with 75 wt% 4,4′,4′-tris(3-methylphenylamino)triphenylamine (MTDATA)/6,6′′-bis(2,4-diphenyl quinoline) (B1PPQ) as an emission source for the WOLED [14]. MTDATA and B1PPQ form the exciplex exhibiting orange emission. The combination of blue molecule emission and orange exciplex emission made white emission of the device. As the thickness of the B1PPQ layer increases, the molecule emission becomes dominant. When the thicknesses of MTDATA and B1PPQ layer were 35 and 7 nm, respectively, the CIE coordinates was (0.35, 0.32) at the applied voltage of 2.5 V. The EL spectrum was sensitive to the applied voltage, and the blue molecule emission becomes dominant at the high applied voltage. G. Grybauskaite-Kaminskiene et al. exploited the trilayer structure of the acceptor/donor/acceptor as the emitting layer [98]. The donor was m-MTDATA and the acceptor was 4,4′-(9H,9′H-[3,3′-bicarbazole]- 9,9′-diyl)bis(3-(trifluoromethyl)benzonitrile) (pCNBCzoCF3) which is a TADF molecule. m-MTDATA and pCNBCzoCF3 form the exciplex exhibiting orange fluorescence and pCNBCzoCF3 exhibits sky-blue fluorescence. The orange and sky-blue emission construct the EL spectrum of the WOLED. The CIE coordinates and maximum EQE were (0.40, 0.44) and 18.8%, respectively. The trilayer structure of the donor/bipolar material/acceptor was also introduced for the WOLED [99]. Two different exciplex emissions were exhibited in the structure. The one is from the donor/bipolar material interface. The other is from bipolar material/acceptor interface. The donor, acceptor, and bipolar material were m-MTDATA, PO-T2T, and 9-(3-(4-Phenylquinolin-2-yl)phenyl)-9H-carbazole (mCzPPQ), respectively. The m-MTDATA:mCzPPQ exciplex exhibits orange fluorescence and the mCzPPQ:PO-T2T exciplex exhibits blue fluorescence, resulting in white EL emission of the device. The CIE coordinates, CRI and maximum EQE were (0.21, 0.56), 52, and 3.15%, respectively.

Figure 9. (a) PL spectra of mCP, TAPC, PO-T2T (solution), mCP:PO-T2T, and TAPC:PO-T2T films; (b) Current efficiency, power efficiency, and EQE as a function of current density for the WOLED of which the molecular orbital energy diagram is depicted as shown in the inset; (c) EL spectra of the WOLED at different applied voltage (ref. [92]).
5.4. Emitting layers incorporating phosphorescent dyes

Phosphorescent dyes were employed for the exciplex-emitting WOLED [55,58,85,92,100–103]. The operating principle of the WOLED is the incomplete energy transfer from blue exciplexes to phosphorescent dyes. In order for the incomplete energy transfer, phosphors were locally doped in the exciplex-forming blended layer or adjacent layers or inserted as a thin layer near the exciplex-forming blended layer. X.-K. Liu et al. reported the WOLEDs with the emitting layer of the blends of 4,4′-bis(9-carbazolyl)-2,2′-dimethylbiphenyl (CDBP)/PO-T2T in which bis(2-phenylpyridine)(acetylacetonate)iridium(III) (Ir(ppy)2acac) and bis(2-methylphenylbenzo[f,h]quinoxaline)(acetylacetone)iridium(III) (Ir(MDQ)2acac) are doped [58]. The CDBP:PO-T2T exciplex emits blue fluorescence of which spectrum is shown in Figure 10(a). Ir(ppy)2acac and Ir(MDQ)2acac emit green and red phosphorescence, respectively. In order for the incomplete energy transfer from the exciplex to the phosphors, the phosphors were doped with low concentration of 0.1 and 0.3 wt% for Ir(ppy)2acac and Ir(MDQ)2acac, respectively. The EL spectrum of the device shows three peaks originated from the exciplex and two phosphors as shown in Figure 10(b). The CIE coordinates and CRI of the device were (0.38, 0.42) and 76, respectively, at 10,000 cd/m². The maximum EQE of the WOLED was 25.5% as shown in Figure 10(c). The trilayer of CDBP:PO-T2T (5 nm)/CDBP:PO-T2T:Ir(ppy)2acac (3 nm)/CDBP:PO-T2T:Ir(MDQ)2acac (8 nm) was also employed for the WOLED with the maximum EQE of 29.4%, CRI of 86, and CIE coordinates of (0.46, 0.43) [101]. The triplet harvesting ability of the exciplex as well as efficiently radiative triplet states of the phosphors help to achieve the high efficiency of the WOLED.

5.5. Emitting layers incorporating fluorescent dyes

WOLEDs with the emitting layer of exciplex-forming blends doped with conventional fluorescent dyes or TADF dyes were also reported [55,101]. The conventional fluorescent dye of Rubrene was doped into mCBP:PO-T2T blends, resulting in the CIE coordinates of (0.309, 0.405) and the EQE of 7.1% of the WOLED [55]. The TADF dye of 1,4-dicyano-2,3,5,6-tetrakis(3,6-diphenylcarbazol-9-yl)benzene (4CzTPN-Ph) was doped into the PO-T2T layer adjacent to the blend, resulting in the CIE coordinates of (0.407, 0.416) and the maximum

![Figure 10](image-url)

(a) Absorption and PL spectra of CDBP, PO-T2T, and CDBP:PO-T2T films; (b) EL spectra of the WOLED at different luminance; (c) EQE as a function of luminance for the blue exciplex-emitting OLED, green phosphorescent OLED, red phosphorescent OLED, and WOLED (ref. [58]).

![Figure 11](image-url)

(a) Device structure of the WOLED; (b) EL spectra of the WOLED at different luminance; (c) EQE and power efficiency as a function of luminance for the exciplex emission-based fluorescent WOLED and hybrid WOLEDs exhibiting exciplex and phosphor emissions (ref. [101]).
Table 2. Characteristics of exciplex emission-based WOLEDs.

| Emitting Structure | Maximum EQE (%) | CIE (x, y) | CRI | Year | Ref. |
|--------------------|----------------|-----------|-----|------|-----|
| TPD:STO(m.r 9:1)  | –              | 0.34,0.48 | –   | 2002 | [87]|
| m-MTDATA:PtCl(m.r 1:1) | 6.5         | 0.46,0.45 | 90  | 2007 | [89]|
| MTDATA:polyethylene (35 nm, w.r 1:3)/B1PPQ (7 nm) | –             | 0.35,0.32 | –   | 2008 | [14]|
| m-MTDATA:Al(DBM)3 (m.r 1:2)/TPD:Bphen(m.r 1:1) | 11.6a       | 0.28,0.34 | 70.6| 2014 | [93]|
| mCP:PO-T2T(1:1)&DTAF:PO-T2T(1:1)a | 11.6a       | 0.28,0.34 | 70.6| 2014 | [93]|
| mCBP:PO-T2T(20 nm,1:1)/4CzTPN-Ph (10 nm) | –             | 0.34,0.42 | –   | 2015 | [55]|
| 0.4 wt% Rubrene:mCBP:PO-T2T(m.r 1:1) | 7.1           | 0.31,0.41 | –   | 2015 | [55]|
| CDBP:PO-T2T(5 nm,1:1)/5wt% Ir(ppy)2acac:CDBP:PO-T2T (3 nm, 4:1)/8wt% Ir(MDQ)2acac:CDBP:PO-T2T (8 nm, 4:1) | 29.4       | 0.46,0.43 | 86  | 2017 | [101]|
| TAPC:PO-T2T(1:1)/DPEPO/mCP:PO-T2T(1:1) | 7.92          | 0.31,0.37 | 84  | 2018 | [92]|
| pCNBCzoCF3/m-MTDATA/pCNBCzoCF3 | –            | –         | –   | –    | –   |

aTandem WOLED.

EQE of 4.8% [55]. Z. Wu employed 2,8-di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenylterracene (TBRb) as the conventional fluorescent dye and the CDBP:PO-T2T exciplex as the exciplex-forming host [101]. The structure of the WOLED is shown in Figure 11(a). The doping concentration of TBRb was just 0.3 wt%, resulting in the white EL emission with the CIE coordinates of (0.335, 0.434) at 500 cd/m² which is shown in Figure 11(b). The maximum EQE of the device was 20.8% as shown in Figure 11(c), which is the highest efficiency for exciplex emission-based fluorescent WOLEDs. The characteristics of the WOLEDs described in section 5 are summarized in Table 2.

6. Conclusion

In this review paper, the basic principles of exciplexes coming from its CT character and the characteristics of OLEDs using exciplexes are explained. Exciplexes show slower radiative transition rate than conventional fluorescent molecules due to their small magnitude of transition dipole moments caused by their CT character, which typically induce the low PLQY. In spite of low PLQY of exciplexes, OLEDs employing exciplexes as emitters have been studied actively due to their potential of achieving the IQE of 100% by virtue of the large RISC efficiency in exciplex-forming systems. The large RISC efficiency could be achieved when the singlet-triplet splitting is small, inducing effective state mixing between singlet and triplet states. Even though the PLQY of the exciplex was reported to be 100%, the performance of OLEDs employing exciplexes is still lacking compared to phosphorescent OLEDs with the EQE over 30%. The more study would be needed to understand the transition rates in exciplex-forming systems from molecular structures. Then, the molecular design for the exciplex with the high PLQY will be available, and it will accelerate the improvement on the performance of the exciplex-emitting OLEDs.

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Disclosure statement

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