Blue exciplex emission and its role as a host of phosphorescent emitter

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ABSTRACT

Electroluminescence (EL) and photoluminescence (PL) characters of a series of blue exciplexes from combinations between three electron acceptors (A) and one electron donor (D) were studied. The emissions of three exciplexes, ranging from sky blue to purple blue, though with quiet different acceptor triplet levels, possess the same thermally activated delayed fluorescence character. Temperature dependence of the PL decay measurement suggests that the long-lived exciplex would be quenched heavily by phonon, while the monomer triplet quenching effect was not the origin of low efficiency. Detailed analysis indicates that the RISC rate could be more affected by the spatial structure of D/A materials and substituent group in the D or A molecules. Trap effect and energy transfer from exciplex to the yellow dopant were also studied.

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1. Introduction

Blue exciplex type organic light emitting diodes (OLEDs) have been studied since 2002 [1–4]. However, most of the device efficiencies were quite low. Recently, in order to improve the external quantum efficiency (EQE) of OLEDs, Adachi and coworkers have proposed a new strategy, i.e., the enhancement of EQE from thermally activated delayed fluorescence (TADF) via reverse intersystem crossing (RISC) process from triplet states to the singlet state [5,6]. In the process of TADF, a small singlet–triplet energy difference ($\triangle E_{(S-T)}$) are needed to thermally activated the triplet states to the singlet state. Based on the TADF mechanism, several highly efficient electroluminescence (EL) emissions resulted from exciplexes formed at the interface between donors (D) and acceptors (A) have been demonstrated [4–8]. Although the blue exciplex also behaves small $\triangle E_{(S-T)}$, efficient blue exciplex based OLEDs rarely reported. The highly efficient exciplex OLEDs only achieved in several donor and acceptor combinations, indicating that some other critical limiting factors exist beyond the TADF mechanism. Most of the reported blue exciplex OLEDs were being remained at a phenomenal stage, suggesting that the development of the blue exciplex EL is still a big challenge. On the other hand, because the emitting layer (EML) with wider band gap must be required, the achievement of blue emission has been little reported to date [1–4].

In this work, we address blue exciplex emission of a series of acceptor components with one donor component. To achieve blue exciplex emission, the donor material with deep highest occupied molecular orbital (HOMO) level and acceptor material with a high lowest unoccupied molecular orbital (LUMO) level are required. In terms of such a consideration, mCP was used as the donor component because its HOMO and LUMO levels are located at 6.1 eV and 2.4 eV, respectively. Three electron-transporting materials, including 4,7-diphenyl-1, 10-phenanthroline (Bphen), 1,3,5-tri(phenyl-2-benzimidazoly)-benzene (TPBi) and 2,4,6-tris (3-(1H-pyrazol-1-yl)phenyl)-1,3,5-triazine (3PT2T), were selected as the acceptor components in the D:A exciplex system. The PL decay characters of these three exciplexes under different temperatures with the monomer triplet quenching effect are systematically studied. The role of our exciplex as phosphor host was also detailed investigated. Based on these studies, we outlined the limiting factors of low efficiency exciplex and gave a comprehensive description of the exciplex-host system.

2. Experimental section

OLED devices were fabricated using pre-cleaned ITO-coated glass substrates with a sheet resistance of 15 Ω/cm^2 and ITO thickness of 150 nm. They were patterned so that the OLED devices had

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a pixel size of about 9 mm². The small molecule and cathode layers were thermally evaporated using the multiple-source organic molecule deposition method. PL spectra of all the films were measured using Hitachi F7000 spectrometer and EL spectra were determined by OPT-2000 spectrophotometer. PL decay times of all the films were measured by FL920. All the EL measurements were carried out at room temperature under ambient condition.

3. Results and discussion

3.1. Formation of blue exciplex and its PL characters

Molecular structures of materials used in forming exciplexes are shown in Fig. 1a. The architecture of our blue exciplex based OLED and the schematic exciplex energy level diagram are indicated in Fig. 1b. All the exciplex based OLEDs comprise a 20 nm co-deposited films of mCP:50 wt.% A, where A denotes Bphen, TPBi and 3PT2T. The EL spectra and device performances of the three exciplex based OLEDs are shown in Fig. 2c,d and listed in Table 1. The PL spectra of the exciplexes are depicted in Fig. 2a. The PL spectrum of mCP:Bphen was red-shifted with respect to that of mCP:TPBi (Fig. 2a and c) though Bphen have a higher HOMO level (2.5 eV) than that of TPBi (2.7 eV). However, the higher LUMO level does not conflict with the experimental result, because the exciplex emitting energy is not only related with the HOMO–LUMO energy gap value but also related with the coulombic binding energy which can be different in different systems. In the previous study, we also found that the m-MTDATA:TPBi and m-MTDATA:Bphen exhibited the reverse energy relation [7]. The PL spectra of the co-deposited films are obviously red-shifted as compared to the PL spectra of either the donor or the acceptor components. In Fig. 2a, the well resolved PL spectra of mCP, Bphen and TPBi exhibited non gaussian distributions, indicating a ππ transitions [9]. On the other hand, the mixed films all exhibited gaussian distributions, suggesting the formation of exciplexes [10]. The PL decay characters of these exciplexes are depicted in Fig. 2b. All the exciplex PL decay curves are composed of two components i.e., a shorter component of ca. 4 ns and a longer component of ca. 20 ns. The PL lifetime of the neat mCP film was determined as ca. 3 ns, as shown in Fig. 2b. And the lifetime of the neat TPBi film is only ca. 1.2 ns [11]. Because the lifetime of D(A) monomer was quenched by A(D) and exciplex to ps level, the two components PL decay character should not result from the overlap of emission

of the D/A and exciplex [12,13]. The character of long component in decay times are quite different from the PL decay character of both the D- and A-components, further demonstrated that the exciplex formed in the D:A mixed film. Therewith, we can confirm that the PL decay of two components should be assigned to the delayed fluorescence based on a TADF mechanism. This conclusion was supported by further study of PL intensities and decays of exciplex under different temperatures, as discussed in the next section.

3.2. Temperature dependence of PL characters and triplet quenching effect in the PL process

To further ascertain whether the aforementioned delayed components in the PL decays of three mixed files were from a thermally activated process, temperature dependence of the PL decay characters for the three exciplexes were explored, as shown in Fig. 3a–c, respectively. The relative PL intensities (defined as PL intensity of three exciplexes divided by the same arbitrary number) of all three exciplexes increased with temperature increasing to about 50 K in Fig. 3d, suggesting not only a thermally activated process but also a small $\triangle E_{S-T}$ between the singlet and triplet states [7,12,13]. It is interesting that the PL intensities of all three exciplexes decreased dramatically with the temperature increasing to above 200 K, indicating that the exciplexes were quenched by phonon at high temperature. Similar result can be found in previous report [5]. One of the main obstacles of the efficient blue exciplex is the monomer triplet quenching effect due to the low acceptor or donor triplet level. In this work, Bphen, TPBi and 3PT2T cover a wide range of triplet levels from 2.5 eV to 2.8 eV [12,14,15]. The triplet energy levels of the three exciplexes of mCP:Bphen, mCP:TPBi and mCP:3PT2T are 3.04 eV, 3.12 eV and 2.78 eV respectively. The triplet levels of exciplexes in mCP:Bphen is higher than the triplet levels of Bphen and mCP, therefore, would be quenched by the monomer triplet states. However, the PL lifetime of the mCP:Bphen was of the same order as mCP:3PT2T for which no quenching effect exist because the triplet level of mCP:3PT2T exciplex is well confined in the combination (a T_1 level of 2.9 eV for mCP) [15,16]. In Fig. 3b and c, the long component decreases with the rising of temperature, especially for mCP:Bphen film, indicating a competition exist between the thermally activated RISC process and the phonon quenching effect. The PL decay profile of mCP:TPBi film was independent of temperature in Fig. 3a, indicating that both the singlet and triplet exciplexes were quenched by the phonon. Nonetheless, all three exciplexes perform universal
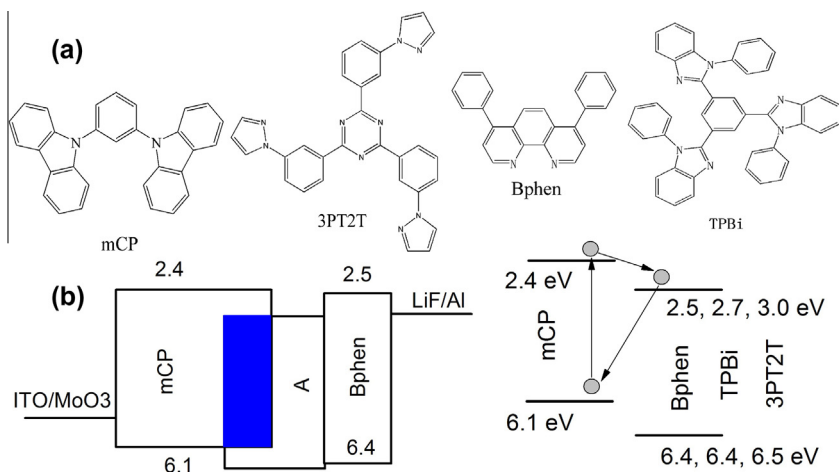

Fig. 1. (a) The molecular structures of 3PT2T, mCP, Bphen and TPBi. (b) Left: device structure of our blue exciplex OLED and right: the schematic exciplex energy level diagram. The device structure is: ITO/mCP (20 nm)/mCP:50 wt.% acceptors (20 nm)/acceptors (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al (80 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
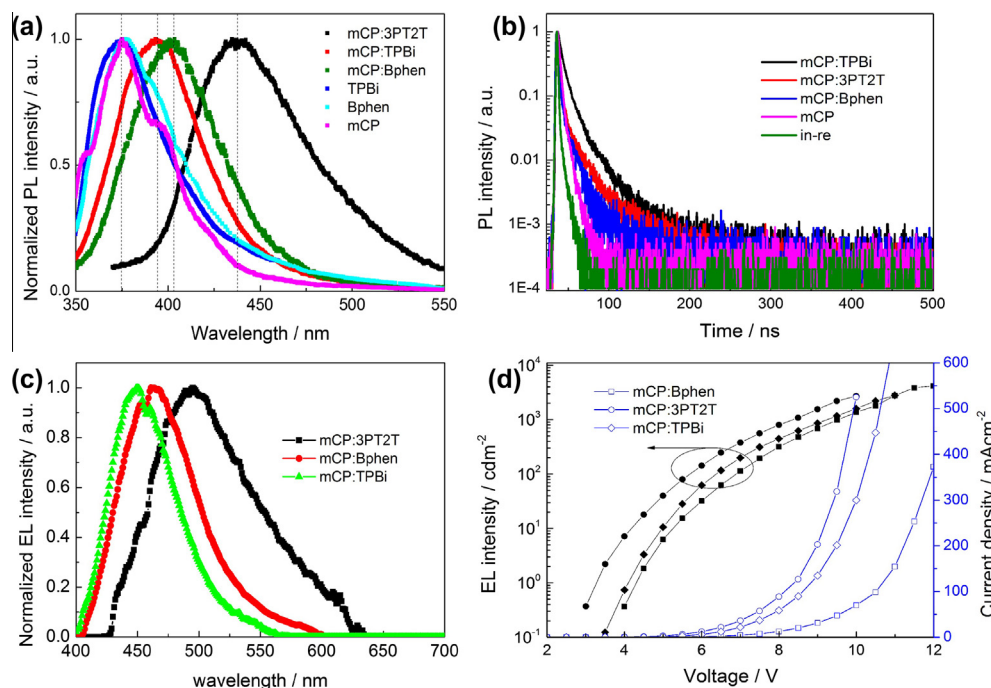
Fig. 2. (a) PL spectra of neat TPBi, Bphen and mCP films, as well as the co-evaporated films of mCP:TPBi, mCP:Bphen and mCP:3PT2T with a 1:1 weight ratio. Excited at 266 nm and monitored at 390 nm, 405 nm and 435 nm respectively. (b) PL decay times of the exciplexes formed at above three mixed films and neat mCP film. The instrumental response (in-re) is also shown with a length of ca. 1.5 ns. (c) EL spectra of OLEDs with mCP:Bphen, mCP:TPBi or mCP:3PT2T blend films at 6 V bias. The EL spectra of OLEDs with mCP:Bphen and mCP:TPBi as emitting layers red-shift/blue-shift as the thickness of electron transporting layer changed. However, no red-shift/blue-shifting occurs as a function of operating bias when the thickness of electron transporting layer is fixed (data not shown here). We speculate that when the recombination zone are located partly at the mCP layer, causing slightly monomer emission from mCP. (d) EL intensity and the current density as a function of the bias for the three exciplex based devices. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
The comparison between the EL performances of the blue exciplex OLEDs.

Acceptor	EL performance parameters					
	Turn-on voltage (V)	Max current efficiency (cd/A)	Max power efficiency (lm/W)	EQE (%)	CIE coordinates	
					X	Y
Bphen	4.3	2.83	1.42	2.23	0.1492	0.1537
TPBi	4.1	1.15	0.66	1.48	0.1456	0.0898
3PT2T	3.2	1.46	1.14	0.57	0.2547	0.3910

shorter PL lifetimes than the fluorescence decay times of the reported efficient exciplexes (hundreds of nanosecond) regardless of the triplet quenching effect existing or not [1,5–8,12,13,17–21]. Therefore, figuring out the limiting factor of the reverse intersystem crossing would be crucial to reveal the mechanism behind the exciplex PL and EL processes.

3.3. Comparison with high efficiency exciplex systems

As discussed above, the short PL decay time did not originate from triplet quenching effect, suggesting that it should be an intrinsic property of the exciplex. To the best of our knowledge, most of the high efficiency exciplexes possess long PL decay character [5–8,22,23]. As shown in Fig. 4a, in comparison to the high efficiency m-MTDATA:Bphen and m-MTDATA:TPBi exciplexes, our exciplexes offer fairly short decay time. Our best blue exciplex device with mCP:Bphen as EML performs an EQE of 2.23%, which is lower than that of the devices using m-MTDATA:Bphen, m-MTDATA:TPBi and TCTA:3PT2T as EML (EQE of 7.9%, 6.8% and 7.8%) [7,8]. To ascertain the origin of the short PL decay character of exciplex, we made a comparison of donor spatial structure between our blue exciplex and high efficiency exciplex with the

same acceptor. The HOMO structures of mCP, m-MTDATA and TCTA are calculated from Gaussian 09 B3LYP with basic set 6-31G*, as shown in Fig. 4b. We found the HOMO of the m-MTDATA and TCTA molecules more populated in the central triphenylamine position while the HOMO of mCP more populated in the peripheral carbonzole positions. The different HOMO population suggests that the planar carbonzole based HOMO structure give a less spin flip probability of triplet exciplex than that of the stereo triphenylamine spatial structures [24–26]. Due to the small spin flip probability of the exciplex, the RISC process could be obviously depressed even with a small $\triangle E_{\text{S-T}}$.

On the other hand, the mCP-based exciplex do give high efficiency in the most recent reports where PO-T2T and HAP-3MF are used as acceptors respectively [4,22]. In our result, no exciplex emission was found in the mCP:T2T (2,4,6-tris(biphenyl-3-yl)-1,3,5-triazine) mixed film. One may argue that the nπ electron in the PO-T2T and 3PT2T gives more spin filp chance as reported in literatures [9,27]. However, we also found that the combinations of m-MTDATA:3PT2T and m-MTDATA:PO-T2T, with both D and A have hetero-atoms (N ,O and P)(Fig. 4c), gave very weak red emissions. So we speculated that the transient dipole between donor and acceptor at least plays a key role in exciplex emission process.

3.4. Blue exciplex as host of yellow phosphor

The OLEDs based on exciplex host doped with the phosphor have been carried out in recent years [23,28–34]. One advantage of exciplex host based device is the low turn-on bias due to directly energy transfer from the exciplex to the dopant molecule. However, the direct evidence for the energy transfer from the exciplex host to the phosphor molecule has not been reported sufficiently [20,23–29]. On the other hand, the trap effect can exist at the same time.
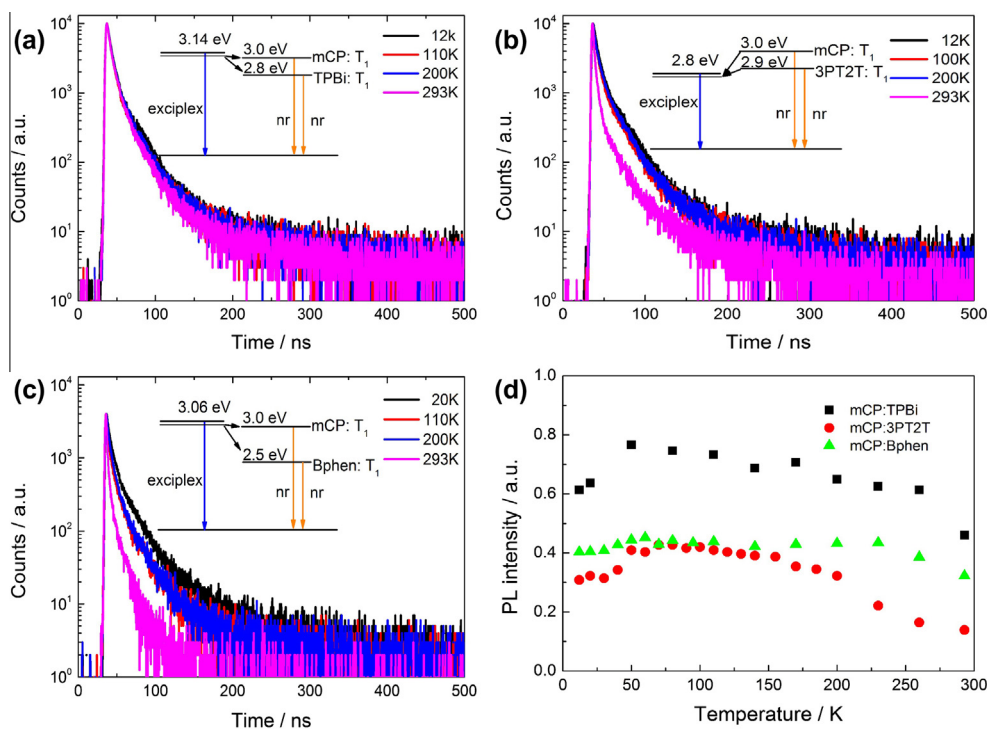
Fig. 3. The temperature dependence of decay characters of (a) mCP:TPBi, (b) mCP:3PT2T and (c) mCP:Bphen mixed films. (d) Relative PL intensity of mCP:Bphen, mCP:TPBi and mCP:3PT2T mixed films as a function of temperature. Excited at 266 nm and monitored at 390 nm, 405 nm and 435 nm respectively. Inset of (a), (b), (c): schematic energy levels of singlet and triplet exciplexes compared with the triplet exciton levels of donor and acceptor monomers.
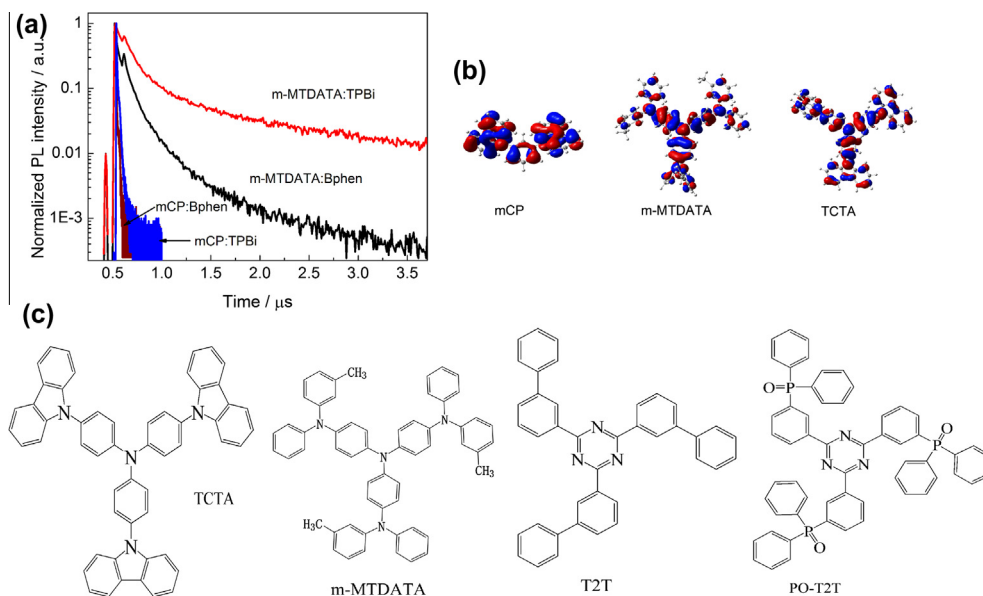

Fig. 4. (a) PL decay characters of mixed films: mCP:Bphen, mCP:TPBi, m-MTDATA:Bphen and m-MTDATA:TPBi. The monitoring wavelength is 405 nm, 395 nm, 525 nm and 560 nm and excitation wavelength is 266 nm, 266 nm, 355 nm and 355 nm, respectively. (b) The HOMO electron structures of mCP, m-MTDATA and TCTA calculated from Gaussian 09 B3LYP with basic set 6-31G*. (c) Chemical structures of m-MTDATA, TCTA, T2T and PO-T2T.

Using bis(2-phenyl-1,3-benzothiozolato-N, C 2′) iridium (acetylacetonate) (Ir(bt)₂(acac)) as the phosphor dopant, we investigated the energy transfer process from exciplex to phosphor dopant [35]. The mCP:3PT2T-exciplex was selected as a representative host because the energy of triplet exciplex can efficiently transfer to the dopant molecules without quenching by monomer triplet states. As expected, our exciplex-host based OLED gave a low

turn-on bias of 2.8 V (Fig. 6a). We have examined the PL features of the doped films composed of mCP, 3PT2T and the D:A exciplex as host, respectively. The PL spectra and decay characters of the three films are displayed in Fig. 5a and b with the PL spectrum of mCP:3PT2T mixed film for comparison. The phosphor doped films emitted the same double peaks of Ir(bt)₂(acac) which is obviously higher than that of mCP, 3PT2T or the exciplex. However, the yellow
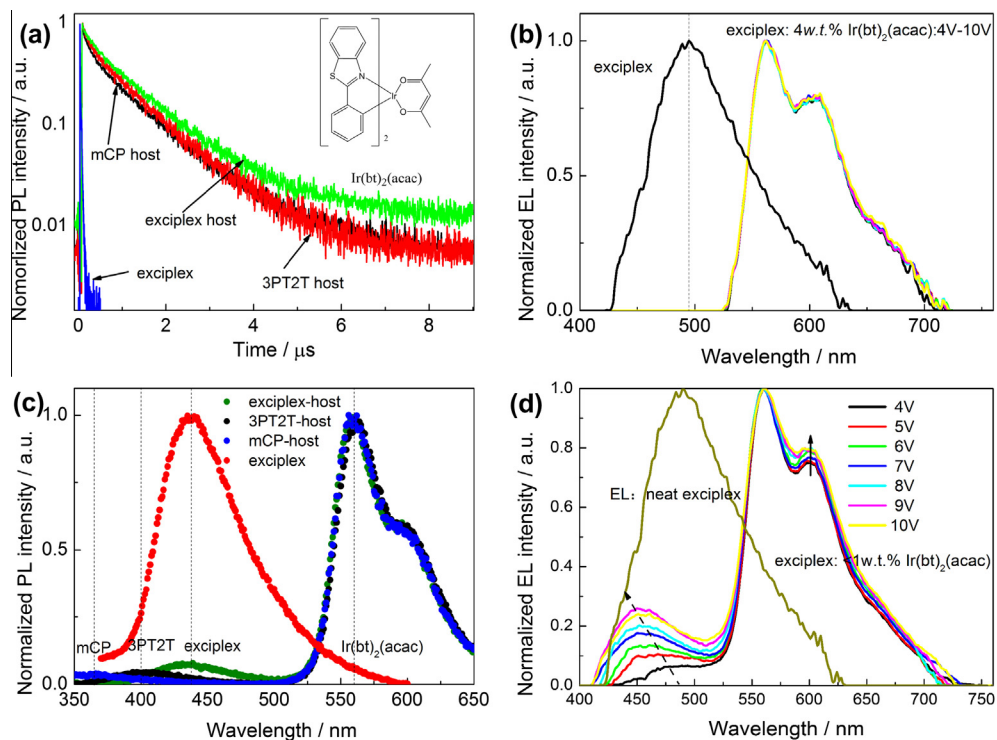
Fig. 5. (a) PL decay characters of Ir(bt)$_2$(acac) doped in mCP, 3PT2T film or in exciplex host with PL decay character of the mCP:3PT2T exciplex for comparison. Excited at 266 nm and monitored at 435 nm and 600 nm for the exciplex and the Ir(bt)$_2$(acac) emission respectively (we the shoulder peak of Ir(bt)$_2$(acac) because the 560 nm peak have a little overlaps with the spectrum of the exciplex). Inset: the molecular structure of Ir(bt)$_2$(acac). (b) PL spectra of Ir(bt)$_2$(acac) in mCP, 3PT2T, and mCP:3PT2T exciplex host with 266 nm excitation wavelength and monitored at 600 nm. EL spectra of exciplex based device with (c) 4 wt.% and (d) <1 wt.% Ir(bt)$_2$(acac) under bias ranging from 4 to 10 V, with the EL spectra of exciplex under a 6 V bias for comparison. The device structure is: ITO/mCP (30 nm)/mCP:3PT2T: <1 wt.% Ir(bt)$_2$(acac) (10 nm)/3PT2T (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al (80 nm).
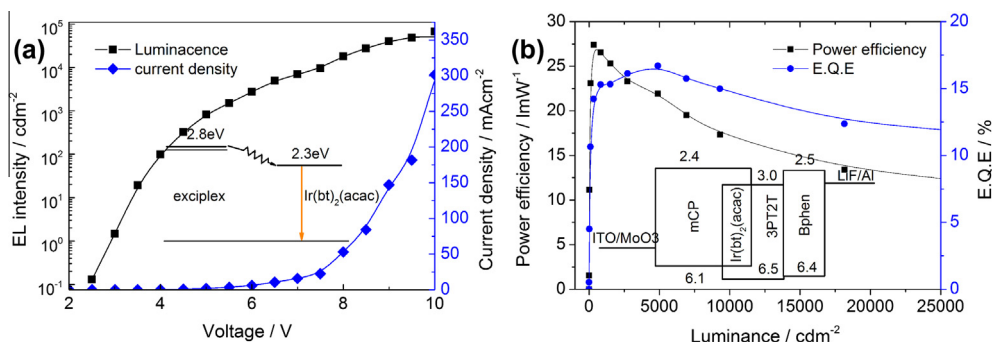

Fig. 6. (a) Luminance and current density vs. bias for the yellow emission device with exciplex host. Inset: the schematic energetic diagram of the energy transfer process from the exciplex to the yellow dopant (Ir(bt)$_2$(acac)). (b) Power efficiency and EQE vs. luminance for the yellow emission device. Inset: the device structure of exciplex host based yellow EL device. The device structure is: ITO/mCP (30 nm)/mCP:3PT2T: 4 wt.% Ir(bt)$_2$(acac) (10 nm)/3PT2T (5 nm)/Bphen (30 nm)/LiF (1 nm)/Al (80 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

emission in doped exciplex films have a longer PL lifetime than that of doped films with mCP or 3PT2T as host (Fig. 5a), indicating a direct energy transfer from exciplex to the phosphor dopant.

Fig. 5c depicts the EL spectra of the devices with mCP:3PT2T as the host and 4.0 wt.% phosphor as the dopant. Different from PL process, the EL spectra shows no exciplex emission at vary operating bias. The absence of exciplex EL peak suggests that the exciplex emission was partly quenched by the dopant with trap effect. When the concentration of phosphor dopant is smaller than 1.0 wt.%, the EL of exciplex was not fully quenched by the phosphor dopant, as shown in Fig. 5d. It is interesting that with increasing of the bias, the spectra of exciplex blue-shift accordingly (Fig. 5d: black dash line arrow). The blue-shift of exciplex spectral peak accompanied by an increase of the shoulder peak of the dopant (Fig. 5d: black line arrow) gives direct evidence of energy transfer from exciplex to the triplet metal–ligand charge transfer states [36]. In addition, exciplex-host based device performs a small EL efficiency roll-off at large current density, since the extra charges could temporally be stored in the exciplex host. Our OLED with an exciplex host provides a small efficiency roll-off of 28% at a high EL luminance of 25,000 cd/m^2 and a high EQE of 16.7%, as shown in Fig. 6a and b. These results consist with the PL efficiency of 65% for Ir(bt)$_2$(acac), correspond with an EQE of 13–19.5% assuming an out coupling efficiency of 20–30% [37].

4. Conclusion

We have studied a series of blue exciplexes with the same electron donor and three different electron acceptors. The exciplexes provide the same short PL decay characters though possess small $\triangle E_{S\text{-}T}$. Detailed analysis of the PL characters of a large amount of exciplexes has been carried out. The results suggest that high monomer triplet level, large transient dipole between D and A and stereo spatial structure of D/A are encouraged. In the end, the PL- and EL-energy transfer processes from the triplet exciplex to the phosphorescent emitter were respectively explored. The dopant quenched the exciplex more seriously in the EL than in the PL process, suggesting that a trap effect also exist in our exciplex-host system. These results are particularly important for developing high efficiency EL materials and the new structured devices.

Acknowledgements

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