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Efficient Triplet Application in Exciplex Delayed-Fluorescence OLEDs Using a Reverse Intersystem Crossing Mechanism Based on a $\Delta E_{\mathrm{S-T}}$ of around Zero

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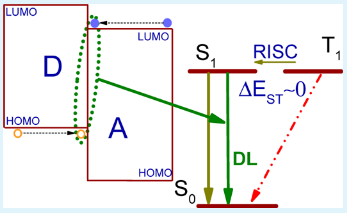
Supporting Information

ABSTRACT: We demonstrate highly efficient exciplex delayed-fluorescence organic light-emitting diodes (OLEDs) in which 4,4′,4″-tris[3-methylphenyl(phenyl)-aminotriphenylamine (m-MTDATA) and 4,7-diphenyl-1,10-phenanthroline (Bphen) were selected as donor and acceptor components, respectively. Our m-MTDATA:Bphen exciplex electroluminescence (EL) mechanism is based on reverse intersystem crossing (RISC) from the triplet to singlet excited states. As a result, an external quantum efficiency (EQE) of 7.79% at 10 mA/cm^2 was observed, which increases by 3.2 and 1.5 times over that reported in *Nat. Photonics* **2012**, *6*, 253 and *Appl. Phys. Lett.* **2012**, *101*, 023306, respectively. The high EQE would be attributed to a very easy RISC process because the energy difference between the singlet and triplet excited states is almost around zero. The verdict was proven by photoluminescence (PL) rate analysis at different temperatures and time-resolved spectral analysis. Besides, the study of the transient PL process indicates that the presence of an unbalanced charge in exciplex EL devices is responsible for the low EQE and high-efficiency roll-off. When the exciplex devices were placed in a 100 mT magnetic field, the permanently positive magnetoelectroluminescence and magnetoconductivity were observed. The magnetic properties confirm that the efficient exciplex EL only originates from delayed fluorescence via RISC processes but is not related to the triplet−triplet annihilation process.



KEYWORDS: *reverse intersystem crossing, delayed fluorescence, exciplex OLED, efficient triplet application*

Because organic light-emitting diodes (OLEDs) have been applied in panel displays and solid-state lightings, various organic electroluminescence (EL) devices and materials have been developed. Especially, the fluorescent and phosphorescent materials and devices have attracted extensive interest.[1,2] It is generally recognized that fluorescence is resulted from singlet exciton, while phosphorescence emission arises from triplet excition, which provides a maximum theoretical internal quantum efficiency (IQE) of 100%.[3] For example, devices with the complex tris(2-phenylpyridinato)iridium(III) [Ir(ppy)$_3$] as the emitter have high efficiency owing to the heavy-atom effect.[4] Although EL devices with iridium complexes could offer high IQE, there are still many disadvantages, such as a serious efficiency roll-off at high current density and high application cost.[5] The fluorescent OLEDs have high working stability but only have a lower maximum IQE of 25%.[6,7]

In view of the above disadvantages in fluorescence and phosphorescence OLEDs, great efforts have been devoted to harvest triplet excited states via reverse intersystem crossing (RISC). RISC of the triplet (T) to singlet (S) excited states require a small energy gap ($\Delta E_{\mathrm{S-T}}$) between the S and T excited states. Usually, there are three typical excited states possessing small $\Delta E_{\mathrm{S-T}}$, i.e., a D/A exciplex, an intramolecular charge-transfer (CT) state, and a dimer state, respectively. Generally, the exciplex state exhibits either a positive or negative $\Delta E_{\mathrm{S-T}}$ value,[8,9] the intramolecular CT state usually has a negative or zero $\Delta E_{\mathrm{S-T}}$ value,[10−13] and the calculated dimer state mostly possesses a lower positive $\Delta E_{\mathrm{S-T}}$ value.[14,15] Recently, the Adachi group first demonstrated a higher external quantum efficiency (EQE) than the fluorescent limit of 5% by using an efficient RISC process based on a thermally activated delayed fluorescence mechanism.[9] The RISC mechanism is considered an up-converted process from the T to S level, and a small $\Delta E_{\mathrm{S-T}}$ value is required.

In this study, we report a strategy to realize more high-efficiency OLEDs via a RISC process. The energy difference ($\Delta E_{\mathrm{S-T}}$) between the S and T excited states in our exciplex device almost even equals zero; i.e., $\Delta E_{\mathrm{S-T}}$ is smaller than that of general delayed fluorescence of the intermolecular exciplex OLEDs. This is a very important route for the material selection and ingenious design of exciplex OLED structures.[16−18] The small $\Delta E_{\mathrm{S-T}}$ value is proven by PL rate analysis at different temperatures and time-resolved spectral analysis,

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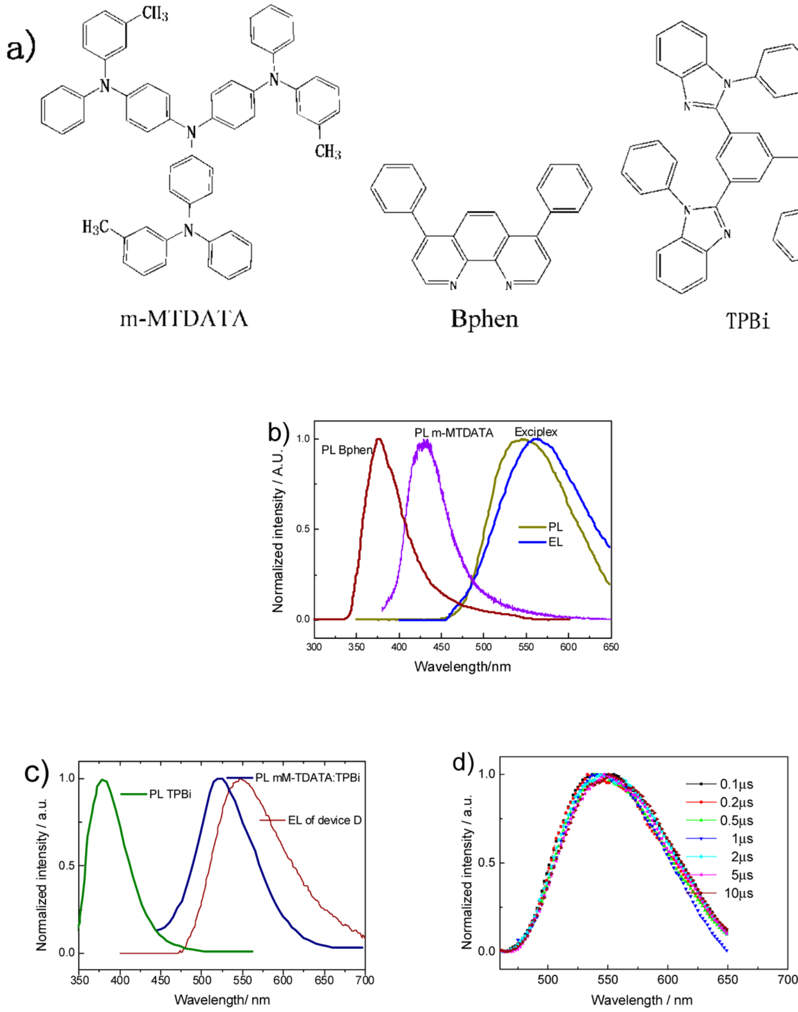

Figure 1. (a) Chemical structures of m-MTDATA, Bphen, and TPBi. (b) Fluorescence spectra of neat m-MTDATA and Bphen films and a m-MTDATA:70 mol % Bphen mixed film at 300 K as well as the EL spectrum of a device with the mixed layer (device A). (c) PL of a neat TPBi film and a m-MTDATA:50 mol % TPBi mixed film at 300 K as well as the EL spectrum of a device with a mixed layer of m-MTDATA:50 mol % TPBi (device D). (d) Time-resolved PL spectrum of a m-MTDATA:70 mol % Bphen mixed film at 77 K.

Table 1. EL Parameters of Devices with Different Structures

	device structure	maximum EQE (%)	maximum EL luminance (cd/m^2)	current efficiency (cd/A)	power efficiency (lm/W) at 10 mA/cm^2	PL efficiency (%)	singlet exciplex formation fraction (%)
device A	ITO/m-MTDATA (27 nm)/m-MTDATA:70 mol % Bphen (23 nm)/Bphen (20 nm)/Alq$_3$ (13 nm)/LiF (1 nm)/Al (80 nm)	7.79	16418	20.90	11.95	15 ± 3	173−260
device B	ITO/m-MTDATA (20 nm)/m-MTDATA:70 mol % Bphen (27 nm)/Bphen (20 nm)/LiF (1 nm)/Al (80 nm)	5.70	10720	17.12	11.62	15 ± 3	127−190
device C	ITO/m-MTDATA (20 nm)/50 mol % m-MTDATA: Bphen (27 nm)/Bphen (20 nm)/LiF (1 nm)/Al (80 nm)	5.49	12812	14.73	9.08	17 ± 3	108−161
device D	ITO/m-MTDATA (30 nm)/m-MTDATA:50 mol % TPBi (17 nm)/TPBi (27 nm)/(BCP) (7 nm)/LiF (1 nm)/Al (80 nm	6.85	7556	18.80	6.10	17 ± 3	134−201

respectively. The maximum EQE of the optimized device is 7.79% at 10 mA/cm^2 with a brightness of 2190 cd/m^2 and a low efficiency roll-off of 41% at 100 mA/cm^2. This result is higher than those reported by refs 9 and 28, in which EQE is 2.50% and 5.00% at 10 mA/cm^2 with efficiency roll-off values of 87% and 80% at 100 mA/cm^2, respectively. Furthermore, the exciplex OLED also provides high EL intensity composed of a current efficiency of 20.90 cd/A, a maximum power efficiency of 12.97 lm/W and a maximum luminance of 16418 cd/m^2. To investigate the limiting factors of the device EQE and its efficiency roll-off, the transient EL characteristics of the devices with various D:A molar ratios and the TPBi device were studied. The results suggest that devices with poor charge balance suffer greatly from singlet exciplex quenching induced by polaron and triplet exciplex states. On the other hand, permanent magnetoelectroluminescence (MEL) and magneto-

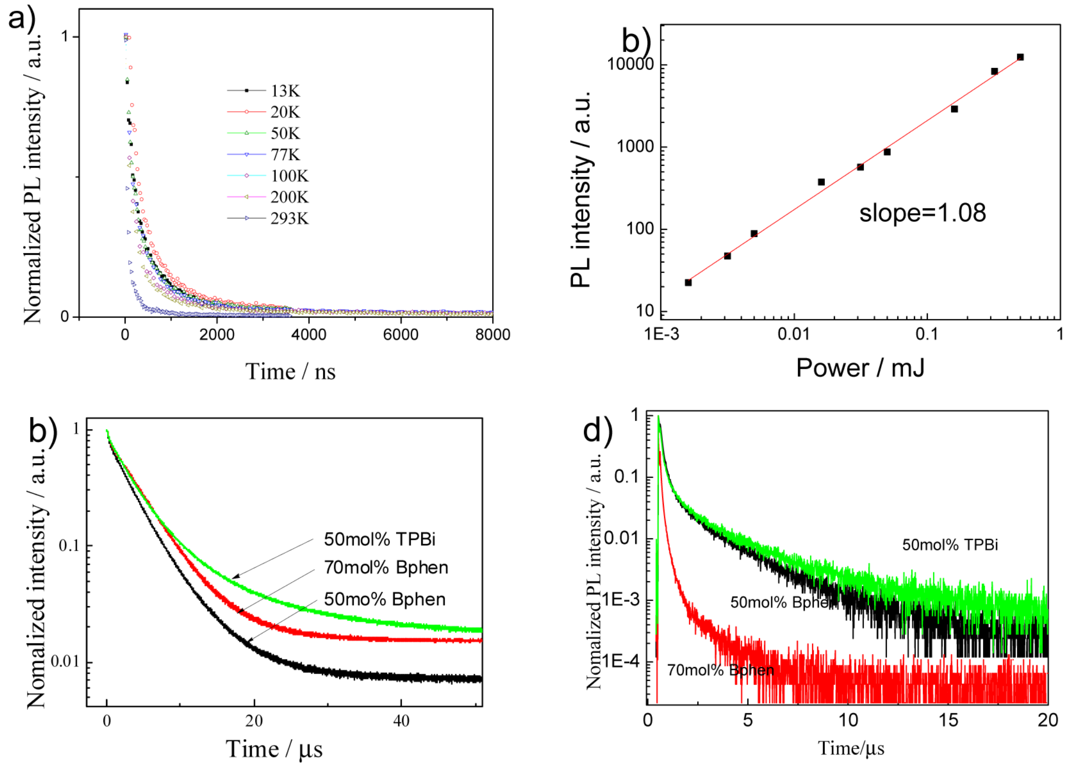

Figure 2. (a) PL decay curves of mixed films of m-MTDATA:70 mol % Bphen at different temperatures and a m-MTDATA:50 mol % TPBi blend film at RT. (b) Exciplex PL intensity dependence on laser fluence under excitation with a 365 nm pulsed laser at RT and with delay and integration times of 10 ns and 10 μs, respectively. (c) EL decay curves of devices A, C, and D under electrical excitation with a 500 ns pulse width, a 1 kHz duty, and 14 V bias. (d) PL decay curves of mixed films of m-MTDATA:70 mol % Bphen and a m-MTDATA:50 mol % TPBi blend film as well as a m-MTDATA:70 mol % Bphen blend film at RT for comparison.

conductivity (MC) of our exciplex device under 100 mT magnetic field were also determined. The experimental results provided that both exciton and exciplex triplet−triplet annihilation (TTA) are not dominant processes but the spin statistic is still out of thermal equilibrium.[19,20]

The chemical structures of 4,4′,4″-tris[3-methylphenyl-(phenyl)aminotriphenylamine (m-MTDATA), 4,7-diphenyl-1,10-phenanthroline (Bphen), and 1,3,5-tris(*N*-phenyl-benzimidazol-2-yl) benzene (TPBi) are shown in Figure 1a. Parts b and c of Figure 1 depict the fluorescence spectra of the mixed films of m-MTDATA:70 mol % Bphen and m-MTDATA:50 mol % TPBi at room temperature (RT) and EL spectra of devices A and D, respectively. The fluorescence spectra of neat m-MTDATA, Bphen, and TPBi films are also shown for comparison. Table 1 listed the device structures and EL performances of devices A−D. Compared to the PL spectrum, the EL spectra are slightly red-shifted. With an increase of the Bphen-to-m-MTDATA molar ratio, a gradual red shift of the EL spectrum of the Bphen devices is observed, as indicated in Figure S1a in the Supporting Information (SI), while at a fixed 70 mol % Bphen molar ratio (device A), a gradual blue shift of the EL spectrum with increasing drive bias was observed (see Figure S1b in the SI). Generally, as the operating bias (i.e., the electrical field) changed, the excitation density could be altered accordingly. Therefore, blue emission originating from the Bphen monomer would contribute to the measured EL spectra with an increase of the bias. In addition, EL excitation is unlike the PL process. That is, the former is produced from a recombination between electrons on the lowest unoccupied molecular orbital (LUMO) of the acceptor ($[\text{LUMO}]_A$) level and holes on the highest occupied molecular orbital (HOMO) of the donor ($[\text{HOMO}]_D$) level, respectively,[21,22] while the latter comes from decay of an intermolecular CT excited state. Both exciplex EL and PL emission are assigned to radiative relaxation from the exciplex excited state to the ground state, and the wavelength peaks can be expressed by the formula

$$h\nu_{(\text{exciplex})\max} \cong I_D - A_A - E_C \tag{1}$$

where I_D and A_A denote the ionization potential of the donor and electron affinity of the acceptor, respectively. E_C expresses the Coulombic attraction energy between D and A species.[23,24]

On the basis of random spin statistics, the PL efficiency of the reported D:A exciplex is generally considered as a criterion for confirming the singlet EL efficiency.[25] When the singlet EL efficiency is larger than 25%, the extra amount arising from the contribution of triplet excitons must be considered. However, this classic method is not always accurate for analysis of the D:A exciplex system. Differing from the PL emission of the D or A component, the exciplex PL emission involves with both donor and acceptor levels. In m-MTDATA:Bphen mixed films, there would be a difference of the CT rate between the D and A singlet excitons and also a difference between the exciplex and D:A monomer exciton. Therefore, the PL efficiency of the mixed film cannot describe the radiative decay rate of the exciplex properly. The PL efficiency with a change in the molar ratio of Bphen/m-MTDATA blend films was measured by using an integrating sphere. When the molar ratio of Bphen in blend films is 20%, 50%, 70%, 80%, and 90%, the PL efficiency of Bphen/m-MTDATA blend films is 26 ± 3%, 17 ± 3%, 15 ± 3%, 13 ± 2%, and 11 ± 2%, respectively. The EQE of the devices, however, is lower for a 20 mol % Bphen device than for a 50 mol % Bphen device. A similar case has also been observed in our previous report.[26] That is, the blend film with a lowest acceptor molar ratio provides the highest exciplex PL efficiency. It is, in general, very difficult to tell whether it is photoluminescence quantum yield (PLQY) or the charge balance ratio that is responsible for the change in the EQE with a change of the concentration. The CT rate of the Bphen exciton is different from that of the m-MTDATA exciton because the overlap between the HOMO levels of Bphen and m-MTDATA is different from that between their LUMO levels.

The EQE of devices generally relies on four factors depending on the formula

$$\mathrm{EQE} = \eta_{\mathrm{out}}\eta_{\mathrm{fl}}\gamma\eta_{\mathrm{fr}} \tag{2}$$

where η_{fr} is the singlet formation ratio and the light-out coupling efficiency (η_{out}) is considered to be 20−30%. The fluorescence efficiency, η_{fl}, has a maximum value of unity; the charge balance factor, γ, can also be assumed to be 1 if we achieve better charge balance. When η_{fl} and EQE are determined from PL measurement and the device performance, we can get the singlet formation ratio

$$\eta_{\mathrm{fr}} = \mathrm{EQE}/\eta_{\mathrm{out}}\eta_{\mathrm{fl}}\gamma \tag{3}$$

Device A with 70 mol % Bphen offers a EQE of 7.79%, and a singlet exciplex formation ratio is situated at a scope of 173.11−259.66%, assuming a light-out coupling efficiency of 20−30%.[27] Even for device C with an EQE of 5.49%, a singlet exciplex efficiency of 107.64−161.47% can still be realized. We also note that PL efficiencies of 26% and 28.5% for m-MTDATA/3TPYMB and m-MTDATA/2,8-bis(diphenylphosphoryl)-dibenzo[*b*,*d*]thiophene (PPT) films have been reported by refs 9 and 28, respectively. The highest EQEs of these two devices are 5.40% and 10%, while their singlet yields are 103.85% and 175.44% (assuming a light-out coupling efficiency of 20%), respectively. Only when the donor and acceptor share the same absorption coefficient and CT rate can the PL efficiency indicate the radiative decay rate of a singlet exciplex, which were neglected in previous reports.[8,9,28]

Figure 2a depicts PL decay curves of blend films with a 70 mol % Bphen at different temperatures. The decay curves involve two decay components even at a very low temperature of 13 K. The PL lifetime parameters at different temperatures are listed in Table 2. With increasing temperature from 13 to 200 K, the composition of the delayed component (about 600−700 ns) was decreased from 38.5 to 23.8% and completely quenched at RT. The time-resolved PL spectrum of the mixed film with 70 mol % Bphen at 77 K is shown in Figure 1d, in which the time range covers both prompt and delayed lifetime components of PL. As the delayed time increased from 100 ns to 10 μs, a slight red shift of the PL spectrum is observed. The small PL red shift and only two components in the PL lifetime within a large temperature range proved the presence of a $\Delta E_{\mathrm{S-T}}$ value of near zero (13 kB ≈ 1.12 meV). As a result, we can conclude that such a RISC process should easily take place and hardly needs the aid of thermal activation. Figure 2b shows a linear relationship between exciplex PL and excitation fluencies in the whole detection time. The linear relationship indicates the absence of a TTA process in our delayed exciplex PL. The argument is further confirmed by the positive MEL and MC results in relative devices.[29]

Table 2. Lifetimes and Percentages of PL Components in a m-MDTATA/70 mol % Bphen Film under 355 nm Excitation (Instrument Response of 8−10 ns)

	component 1		component 2	
temperature/K	time/ns	%	time/ns	%
13	153.1375	0.61468	678.7404	0.38532
20	143.5348	0.64089	664.6802	0.35911
50	121.3562	0.59887	602.6111	0.40113
77	143.9379	0.673 73	721.0313	0.32627
100	106.4493	0.68266	634.8400	0.31734
200	109.0223	0.76200	658.6254	0.23800
293	25.60979	0.79547	181.2463	0.20453

To figure out the limiting factors of the EQE and the origin of the efficiency roll-off, the transient EL characteristics of the devices with various D:A molar ratios and TPBi device systems have been studied. Figure 2c indicates the EL decay curves of devices A, C, and D under electrical excitation with a pulse width of 500 ns, a pulse intensity of 14 V, and a duty of 1 kHz. At the same time, the organic film thicknesses in the above devices have been carefully optimized in order to precisely compare the differences between the decay properties of the four devices. In Figure 2d, the PL decay time is shorter for a 70 mol % Bphen film than for a 50 mol % TPBi film at RT. This indicates that the TPBi device would have a better performance than the Bphen device. The PL efficiency of a 50 mol % TPBi film is about 17%, which is similar to that of a 50 mol % Bphen film but much higher than that of a 70 mol % Bphen film. The changes in the tendency of the PL efficiency in devices with blend layers are quite opposite to those of the EQE (see Table 1). During optimization of the device process, we note that the EL performances are quite sensitive to subtle modulations. From the performances of devices B and C, we speculate that the changes of the layer thickness would modulate the charge-carrier balance. Because the carrier mobilities of m-MTDATA and TPBi are almost identical (ca. 5.0×10^{-5} cm^2/V·s), both are lower than the electron mobility of Bphen (5.0×10^{-4}cm^2/V·s).[30−32] Furthermore, the m-MTDATA film can form ohmic contact with an indium−tin oxide (ITO) anode, but the electrons suffer from a large injection barrier from the cathode to the blend emitting layer.[33] A thick m-MTDATA layer in device D and a thin $\mathrm{Alq_3}$ or BCP layer in devices A and D can further modulate the charge equilibrium and greatly enhance the EL performance. These results suggest that D:A exciplex recombination is a fairly weak process and its decay channels are sensitive to charge balance, which can be influenced by the carrier mobility, D:A molar ratio, layer thickness, and other operation conditions.

Figure 3 shows changes of the EQE, current efficiency, and power efficiency with the current density for Bphen and TPBi devices. From Figure 3 and Table 1, it is observed that the EQE of device A with 70 mol % Bphen is higher than that of 50 mol % TPBi. However, the PL efficiency of a m-MTDATA:70 mol % Bphen film is lower than that of a m-MTDATA:50 mol % TPBi film. It is seen that the PL efficiency of a D:A film deviates far from the radiative decay rate of the exciplex. In Figure 2c and Table 1, the EL decay curve of device D possesses more long delayed components than those of device A, but device D gives lower EL efficiency than device A. To figure out the difference between the microcosmic processes of the two kinds of devices, we further investigated magneto- and nonmagneto-steady-state and -transient EL behaviors of devices A−D, respectively. Figure 4a exhibits the EL profile of device A

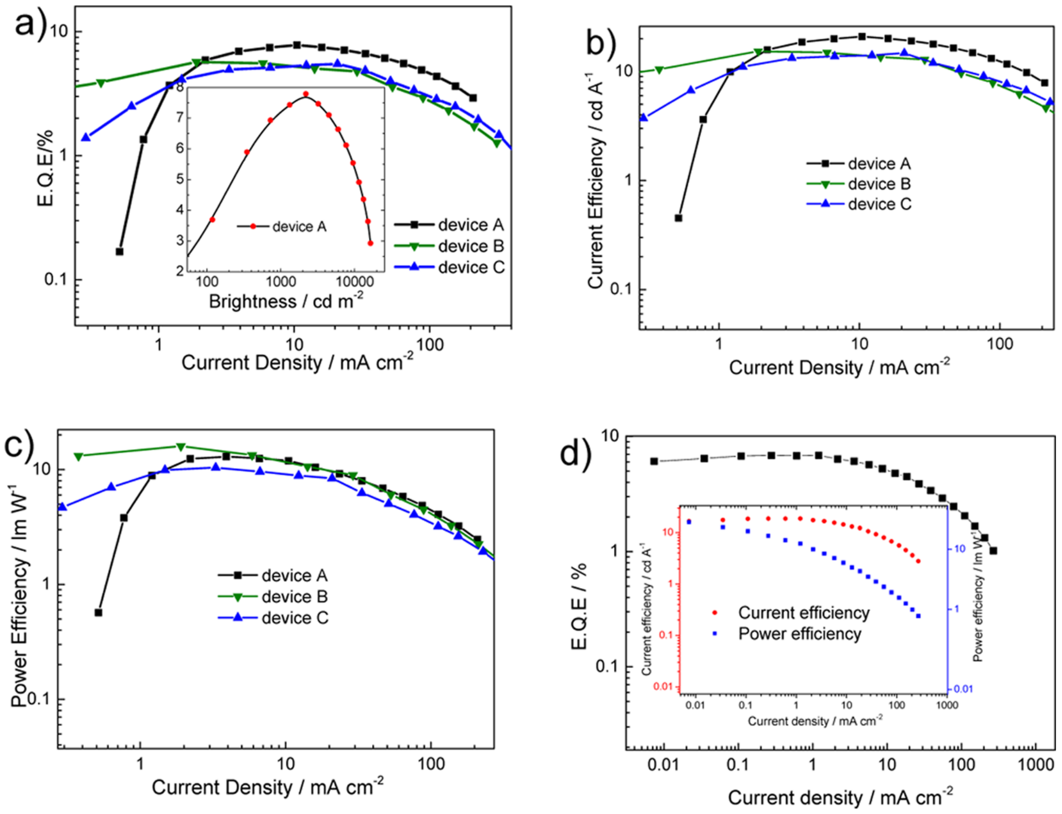

Figure 3. EL characteristics of the OLED devices A−D. (a) EQE versus current density of devices A−C. Inset: EQE versus brightness of device A. (b) Current efficiency versus current density of devices A−C. (c) Power efficiency versus current density of devices A−C. (d) EQE versus current density of device D. Inset: current and power efficiencies versus current density of device D.

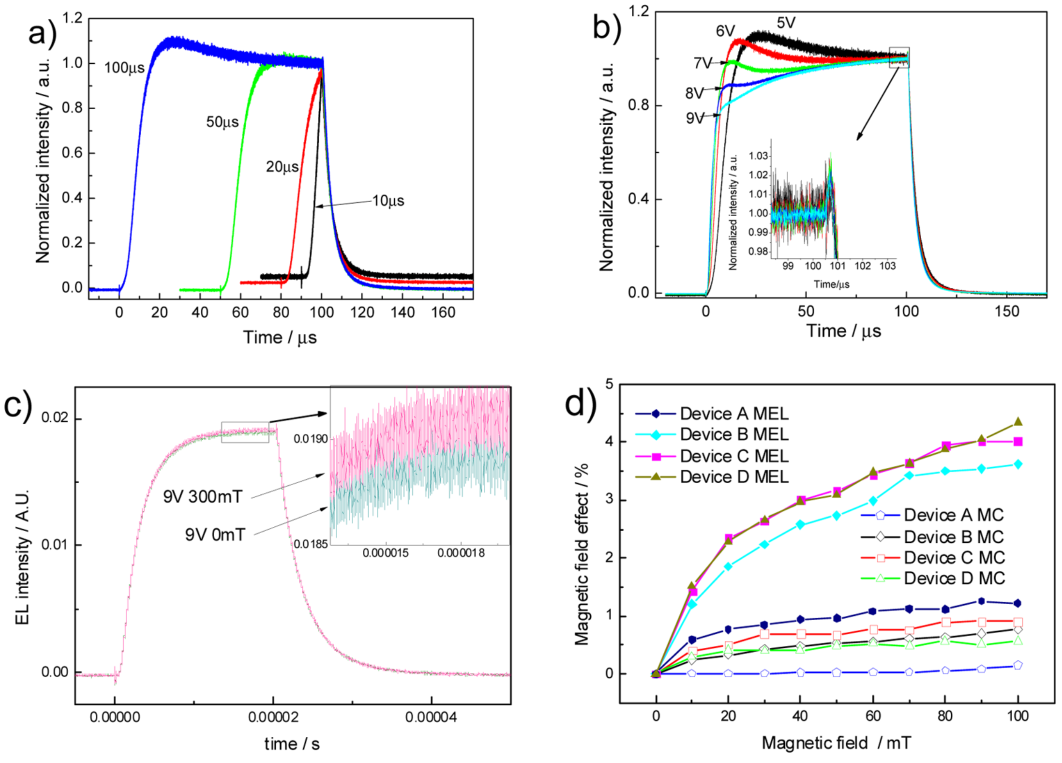

Figure 4. (a) Transient EL intensity of device A as a function of different pulse widths. (b) EL profiles of device A under a 100 μs electrical pulse at different pulse intensities. Inset: turn-off overshoot in the transient EL profile originating from the recombination of space charges. (c) Transient EL profile with and without a 300 mT magnetic field excited by a 20 μs pulse width and a 9 V bias intensity. (d) MEL and MC of devices A−D as a function of the magnetic field intensity at 3 V bias.

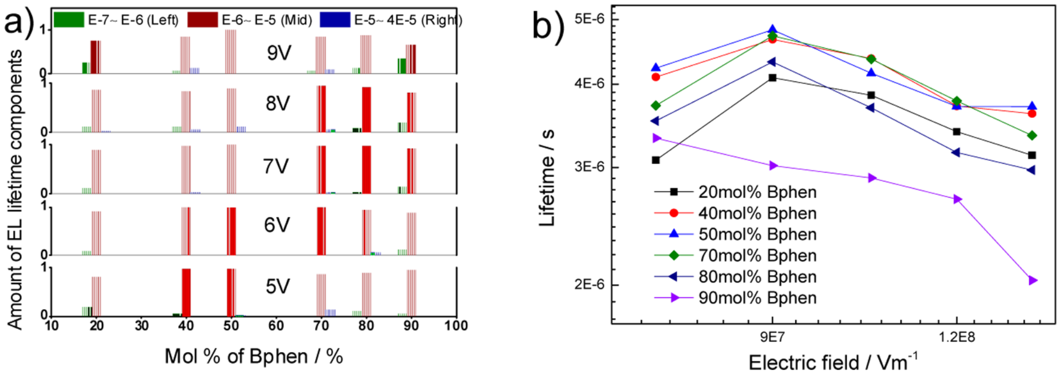

Figure 5. (a) EL lifetime components under electrical excitation with a 20 μs pulse width and different pulse intensities and (b) average EL excited-state lifetimes as a function of the electric field of a device with various molar ratios between m-MTDATA:Bphen in device of ITO/m-MTDATA (20 nm) m-MTDATA: 20−90 mol % Bphen (27 nm)/Bphen (20 nm)/LiF (1 nm)/Al (80 nm).

featuring a long-lived turn-on overshoot and a short-lived turn-off overshoot (inset of Figure 4b). As the pulse width increases from 10 to 100 μs, a more obvious long-lived turn-on overshoot appears. Traditionally, a host−guest system exhibits a long-lived turn-on overshoot arising from carrier traps on the dopant molecules or singlet−triplet annihilation.[34] In addition, the turn-on overshoot from the accumulation of triplet excitons would be retained a very long time and decrease the EL intensity.[35] The turn-off overshoot in the host−guest system usually originates from charge accumulation on emitter molecules.[36,37] Device A shows a long-lived turn-on overshoot, as indicated in Figure 4a. We conjectured that the long-lived turn-on overshoot arises from singlet−triplet annihilation rather than carrier traps on the dopant molecules. When the pulse intensity reaches 9 V, the turn-on overshoot becomes lower than the exciplex EL intensity (Figure 4b) because more unbalanced charges would be injected into the bulk emitting layer under high pulse intensity, which effectively quenches the triplet exciplex states.[35] The turn-on overshoot is not observed in devices B and D because of poor charge balance under low bias. The turn-off overshoot of device A shown in Figure 4b is also observed in devices B and D, which originates from the recombination of trapped charges after pulse turn-off (see the SI combined with Figure S4).[38]

From Figure 4c,d, both MEL and MC retain permanent positive values and monotonously increase with the magnetic field intensity at a low bias of 3 V. MEL should change with either the bias voltage or the current density in TTA conditions. However, all of our devices exhibit positive MEL and MC in the range of 3−9 V, corresponding to a current density between 0 and 100 mA/cm^2 (see Figure S5b in the SI). The result illuminates the presence of a large MEL intensity even in the device with a small ΔE_{S-T}. All of the interaction involving the spin of the particle could be reduced by an applied magnetic field, such as TTA and polaron exciton quenching. To the D:A exciplex system, the polaron can observably quench the long-lived singlet and triplet exciplexes. When singlet and triplet exciplexes contribute to the EL intensity, an applied magnetic field would suppress the quenching effect and positive MEL can be achieved. Both MEL and MC are lower for device A than for device D. This indicates that heavy polaron quenching of the singlet and triplet exciplexes exists in device D because of poor charge balance.[36,39,40] The poor charge balance also leads to a larger efficiency roll-off, as shown in Figure 3d. Meanwhile, the large permanent positive values of MEL and MC imply that the poloron exciplex interaction is a dominant process in our D:A system, while the TTA process at least is not a significant decay channel for the triplet exciplex state.[41]

To understand the effect of the molar ratio of Bphen on the charge balance in the bulk-heterojunction device, we further studied the transient EL behavior of the devices with different m-MTDATA-to-Bphen molar ratios. All of the transient EL processes exhibit the same characteristics with an average lifetime of ca. 0.3−0.5 μs, and the representative results are shown in Figure S4a in the SI (also see Figure 2c). In a comparison of all of the EL results under different pulse biases, subtle differences in the decay curves could be obtained as follows. (a) Exciplex EL suffers from poor charge balance in the devices with 50−70 mol % Bphen. Under electrical excitation of a 20 μs electrical pulse, the EL lifetimes contain a hundreds of nanoseconds decay component, which comes from exciplex scattering induced by free polarons (Figure 5a). (b) Because devices with 50−70 mol % Bphen are excited by a 20 μs electrical pulse, a microsecond component is found in all device EL decay curves. The long component originates from exciplex scattering induced by trapped polarons. (c) The average decay times of all devices are shortened under a high pulse intensity. These results tell us that a high electric field provides a large amount of space charge, resulting in a fast decay of exciplex EL (Figure 5b).

In conclusion, two series exciplex devices consisting of m-MTDATA:Bphen and m-MTDATA:TPBi mixed films based on the RISC mechanism were addressed. A maximum EQE of 7.79% for the optimized device with m-MTDATA:70 mol % Bphen was extracted. The EQE was increased by 3.2 and 1.5 times at 10 mA/cm^2 over that reported by refs 9 and28, respectively. The achievement of high efficiency is mainly ascribed to a ΔE_{S-T} value of around zero. Besides, the study on the transient EL process reveals the presence of unbalanced charge in excited exciplex EL devices so that low EQE and serious efficiency roll-off are observed. From a comparison of the exciplex PL and EL processes, we found that intermolecular exciplex emission is quite sensitive to the charge imbalance. The charge imbalance can arise from the difference between the hole and electron carrier mobility, D:A molar ratio, layer thickness, and other operation conditions. The EL device with poor charge balance suffers greatly from singlet exciplex quenching induced by polaron and triplet states. Positive MEL and MC of our devices suggest that the TTA process is not a significant decay channel of triplet exciplex states. Large MEL indicates that heavy polaron quenching of the singlet and triplet exciplexes is responsible for large efficiency roll-off in the TPBi device. Our studies could open a new development route for the design of a new type of exciplex OLED and selection of new materials for a delayed-fluorescence device based on the RISC mechanism.

■ EXPERIMENTAL SECTION

OLED devices were fabricated using precleaned ITO-coated glass substrates with a sheet resistance of 15 Ω/cm^2 and an ITO thickness of 150 nm. They were patterned so that the OLED devices had a pixel size of 9 mm^2. The small molecule and cathode layers were thermally evaporated using the multiple-source organic molecule deposition method. PL spectra and efficiency of all of the films and EL spectra were determined by a FLS9800 fluorescence spectrometer.

PLQY measurements were carried out using a simplified method developed by Pålsson and Monkman.[42] The thicknesses of all measured organic films were 100 nm. Measurement errors were evaluated from film degradation and system error.

After fabrication, the devices were immediately placed on a Teflon stage between the poles of an electromagnet for both EL and MEL (also MC) transient and steady-state measurements. The magnetic field was perpendicular to the current. In the steady-state measurement, a Keithley 2612 sourcemeter was used to provide a constant voltage from one channel. The light output of the devices was collected by a lens coupled with an optic fiber (2 m) connected to a Hamamatsu photomultiplier. The photomultiplier was placed far away from the electromagnet and was connected to another channel of the Keithley 2612 sourcemeter to record the EL intensity signals. The setup of the transient test was the same as that in our previous works.[10,41] All of the EL measurements were carried out at RT under ambient conditions. It should be mentioned that the performance drifts of the devices are negligible during transient measurement, while the drift could not be ignored during the steady-state test.

In order to minimize the influence from the EL drift, we used a procedure similar to that introduced by Desai et al. in which the zero-field EL was inserted before and after the *B*-field EL measurement.[43] Then MEL was calculated by the formula

$$\text{MEL} = \Delta\text{EL}/\text{EL} = [\text{EL}(B, N) - \text{EL}(0, N)]/\text{EL}(0, N)$$

where $\text{EL}(B,N)$ is the *B*-field EL intensity in the *N*th step and $\text{EL}(0,N)$ is the average value of the two zero-field ELs $[\text{EL}(0,N_1)$ and $\text{EL}(0,N_2)]$. Exemplary data of primary measurements of MEL and MC are depicted in Figure S5 in the SI.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of EL spectra of the devices and PL spectra of the films, current−voltage characteristics of the devices, transient EL features, and experimental data of MFE measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Baldo, M. A.; Forrest, S. R.; Thompson, M. E. In *Organic Electro-Luminescence*; Kafafi, Z. H,, Ed.; Taylor & Francis Group, CRC Press: Boca Raton, FL, 2005.

(2) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. Highly Efficient Phosphorescent Emission from Organic Electroluminescent Devices. *Nature* **1998**, *395*, 151−154.

(3) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. Nearly 100% Internal Phosphorescence Efficiency in an Organic Light-Emitting Device. *J. Appl. Phys.* **2001**, *90*, 5048−5051.

(4) Birks, J. B. *Photophysics of Organic Molecules*; Wiley: New York, 1970; p 372.

(5) Baldo, M. A.; Adachi, C.; Forrest, S. R. Transient Analysis of Organic Electrophosphorescence. Ii. Transient Analysis of Triplet−Triplet Annihilation. *Phys. Rev. B* **2000**, *62*, 10967−10977.

(6) Rothberg, L. J.; Lovinger, A. J. Status of and Prospects for Organic Electroluminescence. *J. Mater. Res.* **1996**, *11*, 3174−3187.

(7) Tsutsui, T.; Saito, S. Organic Multilayer-Dye Electroluminescent Diodes—Is There Any Difference with Polymer Led? *Intrinsically Conducting Polymers: An Emerging Technology*; Springer: Berlin, 1993; pp 123−134.

(8) Park, Y. S.; Kim, K. H.; Kim, J. J. Efficient Triplet Harvesting by Fluorescent Molecules through Exciplexes for High Efficiency Organic Light-Emitting Diodes. *Appl. Phys. Lett.* **2013**, *102*, 153306−153310.

(9) Goushi, K.; Yoshida, K.; Sato, K.; Adachi, C. Organic Light-Emitting Diodes Employing Efficient Reverse Intersystem Crossing for Triplet-to-Singlet State Conversion. *Nat. Photonics* **2012**, *6*, 253−258.

(10) Dias, F. B.; Bourdakos, K. N.; Jankus, V.; Moss, K. C.; Kamtekar, K. T.; Bhalla, V.; Santos, J.; Bryce, M. R.; Monkman, A. P. Triplet Harvesting with 100% Efficiency by Way of Thermally Activated Delayed Fluorescence in Charge Transfer Oled Emitters. *Adv. Mater.* **2013**, *25*, 3707−3714.

(11) Endo, A.; Ogasawara, M.; Takahashi, A.; Yokoyama, D.; Kato, Y.; Adachi, C. Thermally Activated Delayed Fluorescence from Sn4^{+}−Porphyrin Complexes and Their Application to Organic Light Emitting Diodes—a Novel Mechanism for Electroluminescence. *Adv. Mater.* **2009**, *21*, 4802−4806.

(12) Endo, A.; Sato, K.; Yoshimura, K.; Kai, T.; Kawada, A.; Miyazaki, H.; Adachi, C. Efficient up-Conversion of Triplet Excitons into a Singlet State and Its Application for Organic Light Emitting Diodes. *Appl. Phys. Lett.* **2011**, *98*, 083302−083306.

(13) Sato, K.; Shizu, K.; Yoshimura, K.; Kawada, A.; Miyazaki, H.; Adachi, C. Organic Luminescent Molecule with Energetically Equivalent Singlet and Triplet Excited States for Organic Light-Emitting Diodes. *Phys. Rev. Lett.* **2013**, *110*, 247401−247405.

(14) Segal, M.; Singh, M.; Rivoire, K.; Difley, S.; Van Voorhis, T.; Baldo, M. Extrafluorescent Electroluminescence in Organic Light-Emitting Devices. *Nat. Mater.* **2007**, *6*, 374−378.

(15) Difley, S.; Beljonne, D.; Van Voorhis, T. On the Singlet−Triplet Splitting of Geminate Electron−Hole Pairs in Organic Semiconductors. *J. Am. Chem. Soc.* **2008**, *130*, 3420−3427.

(16) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-Emitting Diodes from Delayed Fluorescence. *Nature* **2012**, *492*, 234−239.

(17) Tanaka, H.; Shizu, K.; Miyazaki, H.; Adachi, C. Efficient Green Thermally Activated Delayed Fluorescence (Tadf) from a Phenoxazine−Triphenyltriazine (Pxz−Trz) Derivative. *Chem. Commun.* **2012**, *48*, 11392−11394.

(18) Nakagawa, T.; Ku, S.-Y.; Wong, K. T.; Adachi, C. Electroluminescence Based on Thermally Activated Delayed Fluorescence

Generated by a Spirobifluorene Donor−Acceptor Structure. *Chem. Commun.* **2012**, *48*, 9580−9582.

(19) Jankus, V.; Chiang, C. J.; Dias, F.; Monkman, A. P. Deep Blue Exciplex Organic Light-Emitting Diodes with Enhanced Efficiency; P-Type or E-Type Triplet Conversion to Singlet Excitons? *Adv. Mater.* **2013**, *25*, 1455−1459.

(20) Bobbert, P.; Nguyen, T.; Van Oost, F.; Koopmans, v. B.; Wohlgenannt, M. Bipolaron Mechanism for Organic Magnetoresistance. *Phys. Rev. Lett.* **2007**, *99*, 216801−216804.

(21) Shirota, Y.; Kobata, T.; Noma, N. Starburst Molecules for Amorphous Molecular Materials. 4,4′,4″-Tris(*N*,*N*-Diphenylamino) Triphenylamine and 4,4′,4″-Tris[*N*-(3-Methylphenyl)-*N*-Phenylamino] Triphenylamine. *Chem. Lett.* **1989**, *18*, 1145−1148.

(22) Cecchini, M.; Piazza, V.; Beltram, F.; Lazzarino, M.; Ward, M.; Shields, A.; Beere, H.; Ritchie, D. High-Performance Planar Light-Emitting Diodes. *Appl. Phys. Lett.* **2003**, *82*, 636−638.

(23) Cocchi, M.; Virgili, D.; Sabatini, C.; Kalinowski, J. Organic Electroluminescence from Singlet and Triplet Exciplexes: Exciplex Electrophosphorescent Diode. *Chem. Phys. Lett.* **2006**, *421*, 351−355.

(24) Horváth, A.; Stevenson, K. L. Transition Metal Complex Exciplexes. *Coord. Chem. Rev.* **1996**, *153*, 57−82.

(25) Pope, M.; Kallmann, H.; Magnante, P. Electroluminescence in Organic Crystals. *J. Chem. Phys.* **1963**, *38*, 2042−2043.

(26) Wang, D.; Li, W.; Chu, B.; Liang, C.; Hong, Z.; Li, M.; Wei, H.; Xin, Q.; Niu, J.; Xu, J. Effect of Exciplex Formation on Organic Light Emitting Diodes Based on Rare-Earth Complex. *J. Appl. Phys.* **2006**, *100*, 024506−0245011.

(27) Smith, L.; Wasey, J.; Barnes, W. L. Light Outcoupling Efficiency of Top-Emitting Organic Light-Emitting Diodes. *Appl. Phys. Lett.* **2004**, *84*, 2986−2988.

(28) Goushi, K.; Adachi, C. Efficient Organic Light-Emitting Diodes through up-Conversion from Triplet to Singlet Excited States of Exciplexes. *Appl. Phys. Lett.* **2012**, *101*, 023306−023309.

(29) Graves, D.; Jankus, V.; Dias, F. B.; Monkman, A. Photophysical Investigation of the Thermally Activated Delayed Emission from Films of M-Mtdata: Pbd Exciplex. *Adv. Funct. Mater.* **2013**, *24*, 2343−2348.

(30) Naka, S.; Okada, H.; Onnagawa, H.; Tsutsui, T. High Electron Mobility in Bathophenanthroline. *Appl. Phys. Lett.* **2000**, *76*, 197−199.

(31) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. Multilayered Organic Electroluminescent Device Using a Novel Starburst Molecule, 4,4′,4′′-Tris(3-Methylphenylphenylamino) Triphenylamine, as a Hole Transport Material. *Appl. Phys. Lett.* **1994**, *65*, 807−809.

(32) Hung, W. Y.; Ke, T. H.; Lin, Y. T.; Wu, C. C.; Hung, T. H.; Chao, T. C.; Wong, K. T.; Wu, C. I. Employing Ambipolar Oligofluorene as the Charge-Generation Layer in Time-of-Flight Mobility Measurements of Organic Thin Films. *Appl. Phys. Lett.* **2006**, *88*, 064102−064104.

(33) Iwata, S.; Tanaka, J.; Nagakura, S. Phosphorescence of the Charge-Transfer Triplet States of Some Molecular Complexes. *J. Chem. Phys.* **1967**, *47*, 2203−2207.

(34) Ma, C.; Lengyel, O.; Kovac, J.; Bello, I.; Lee, C.; Lee, S. Time-Resolved Transient Electroluminescence Measurements of Emission from Dcm-Doped Alq3 Layers. *Chem. Phys. Lett.* **2004**, *397*, 87−90.

(35) Zhang, Y.; Whited, M.; Thompson, M. E.; Forrest, S. R. Singlet−Triplet Quenching in High Intensity Fluorescent Organic Light Emitting Diodes. *Chem. Phys. Lett.* **2010**, *495*, 161−165.

(36) Young, R. H.; Tang, C. W.; Marchetti, A. P. Current-Induced Fluorescence Quenching in Organic Light-Emitting Diodes. *Appl. Phys. Lett.* **2002**, *80*, 874−876.

(37) Weichsel, C.; Burtone, L.; Reineke, S.; Hintschich, S. I.; Gather, M. C.; Leo, K.; Lüssem, B. Storage of Charge Carriers on Emitter Molecules in Organic Light-Emitting Diodes. *Phys. Rev. B* **2012**, *86*, 075204−075213.

(38) Liu, R.; Gan, Z.; Shinar, R.; Shinar, J. Transient Electroluminescence Spikes in Small Molecular Organic Light-Emitting Diodes. *Phys. Rev. B* **2011**, *83*, 245302−245312.

(39) Baldo, M. A.; Holmes, R. J.; Forrest, S. R. Prospects for Electrically Pumped Organic Lasers. *Phys. Rev. B* **2002**, *66*, 035321−035336.

(40) Kozlov, V.; Burrows, P.; Parthasarathy, G.; Forrest, S. Optical Properties of Molecular Organic Semiconductor Thin Films under Intense Electrical Excitation. *Appl. Phys. Lett.* **1999**, *74*, 1057−1059.

(41) Peng, Q.; Chen, P.; Li, F. The Charge-Trapping and Triplet−Triplet Annihilation Processes in Organic Light-Emitting Diodes: A Duty Cycle Dependence Study on Magneto-Electroluminescence. *Appl. Phys. Lett.* **2013**, *102*, 023301−023305.

(42) Pålsson, L.-O.; Monkman, A. P. Measurements of Solid-State Photoluminescence Quantum Yields of Films Using a Fluorimeter. *Adv. Mater.* **2002**, *14*, 757−758.

(43) Desai, P.; Shakya, P.; Kreouzis, T.; Gillin, W.; Morley, N.; Gibbs, M. Magnetoresistance and Efficiency Measurements of Alq3-Based Oleds. *Phys. Rev. B* **2007**, *75*, 094423−094427.