Chapter 5
Control of the Triplet Concentration in Organic Light-Emitting Devices

The vivid interest in organic semiconductor materials is stimulated by the technological aspects of applications that employ these new materials in OLEDs [23, 27], thin-film field-effect transistors [93–95], solar cells [82] and biological sensors. Some products, such as emissive OLED displays, [28] have gained rapid acceptance in portable displays because of their bright emission and low power consumption. The remarkable technological breakthroughs in the development of highly efficient OLEDs and the demonstration of optically-pumped lasing [56, 90] using the same class of organic semiconductors have focused an increasing interest in the prospects for making electrically-pumped organic solid-state lasers [85, 86]. However, as discussed in Chap. 1 (Sect. 1.3.4), the combination of several issues makes electrical excitation a particularly tough problem for organic semiconductor lasers. One of the main problems associated with electrically pumped organic semiconductor lasers and other high-brightness organic light sources is the inevitable population and accumulation of triplet excitations, which result in excessive triplet-state losses, such as triplet-triplet absorption [223, 228] and singlet-triplet annihilation [50, 212, 215].

In this chapter, two different approaches to reduce the triplet concentration in organic light-emitting devices are discussed. A first method to control triplet accumulation is by operating the device under pulsed excitation [228]. This is the subject of Sect. 5.1. The behavior of OLEDs with field-effect-assisted electron transport is analyzed under pulsed excitation and their performance is compared to conventional OLEDs using the same materials. If the transit time of carriers through transport layers contributes to the determination of the minimum pulse duration applicable to an OLED, it is expected that devices employing an enhanced field-effect mobility may allow shorter pulse durations compared to standard OLEDs. Section 5.2 then focuses on an alternative way to control the triplet concentration. Polymer films doped with appropriate triplet scavengers are studied by time-resolved photoluminescence measurements. Vertical as well as nonvertical triplet scavengers are investigated and their use for triplet reduction in organic light-emitting devices is argued. The content of this chapter has been published in two different articles [293, 294].

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5.1 Pulsed Excitation of OLEDs with Field-Effect Electron Transport

In literature, pulsed operation is suggested as being one of the approaches to reduce triplet-state losses in organic light-emitting devices [225, 226]. Pulsed excitation makes it possible to separate singlet excitons from triplet excitons in the time domain, allowing a tremendous reduction of the triplet concentration and associated losses in an electrically driven organic light-emitting device [228]. In addition, pulsed operation avoids heat and stress in the device [227] and it allows higher current densities compared to continuous wave (CW) operation [209]. In this section, the behavior of OLEDs with field-effect-assisted electron transport under pulsed excitation is investigated.

5.1.1 Pulse-Width Dependence of Organic Light-Emitting Devices

The devices used in this study comprised 50 nm PTAA as the hole-transporting layer, 20 nm Alq_3:DCM_2 as the light-emitting layer and 50 nm PTCDI-$C_{13}H_{27}$ as the electron-transporting layer. Standard OLEDs as well as OLEDs with field-effect-assisted electron transport were fabricated. The devices were characterized in an inert N_2 atmosphere immediately after evaporation of the metallic top-contact. An Agilent 8114A pulse generator (rise and fall time = 8 ns) was used to apply rectangular pulses to the devices. The duty cycle was 10%, and the pulse length was varied between 100 ns and 100 μs. All coax cables were 50 Ω terminated to avoid reflections. A calibrated integrated sphere (SphereOptics Hoffman GmbH) coupled to an Agilent 4156C parameter analyzer was used for light intensity measurements.

Figure 5.1 shows the measured peak light intensity as a function of the pulse width for a conventional OLED and an OLED with field-effect-assisted electron transport biased at, respectively, 7 V and 20 V. Both devices were fabricated during the same evaporation runs and use the same organic layer stack. From Fig. 5.1 the minimum pulse width that can be applied without affecting the light output can be determined. Both devices allow pulse widths down to $\sim$10 μs without significant reduction of the light intensity. The shape of the curves, however, differs strongly. The OLED with field-effect electron transport exhibit a significantly weaker dependence on the pulse duration compared to the conventional OLED.

Note that the minimum pulse width that can be applied without significant reduction of the light intensity is much shorter than the typical triplet lifetime of fluorescent materials (milliseconds to seconds [230]), indicating that pulsed excitation is useful to reduce the accumulation of triplets in these devices. Indeed, when the pulse repetition rate is sufficiently low and pulses shorter than the lifetime of triplet excitons are applied, the build-in of triplets can be reduced.

If the transit time of the carriers through the organic layers contributes to the determination of the minimum pulse duration, it is expected that OLEDs with field-effect-assisted electron transport, which employ an enhanced field-effect mobility,

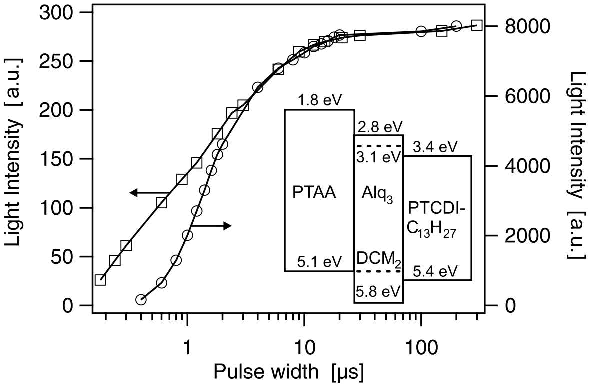


Fig. 5.1 The measured peak light intensity as a function of the pulse width for a conventional OLED (*open circles*) and an OLED with field-effect-assisted electron transport (*open squares*) biased, respectively, at 7 V and 20 V. *Inset*: energy level diagram of the organic layer stack under flat band conditions. The *dotted lines* indicate the HOMO and LUMO positions of DCM_2. (© 2010 IEEE)

could allow shorter pulse durations compared to standard OLEDs. In this way, a more effective reduction of the triplet concentration would be possible when operating the device under pulsed excitation. However, Fig. 5.1 clearly shows that there is no distinct difference between the minimum allowable pulse width without reduction of the light intensity of both device architectures.

5.1.2 Effects Influencing the Pulsed Excitation Behavior of OLEDs

Charge Transport

Different effects may influence the pulse-width dependence of organic light-emitting devices. A first possible reason for the decrease of the light output at short pulse widths could be the finite transit time of the charge carriers through the transport layers. One of the parameters controlling this process is the charge carrier mobility. If the mobility of one of the charge carriers is too low, the steady-state exciton concentration cannot be reached within the pulse duration, resulting in a decrease of the measured light intensity.

To verify whether the charge transport through the electron accumulation layer in PTCDI-$C_{13}H_{27}$ is a limiting factor, OLEDs with field-effect electron transport having different distances between the metallic contact and the insulator edge, and thus different transit times, were fabricated. The result is presented in Fig. 5.2(a): all devices showed the same pulse-width dependence.

Subsequently, it was verified whether charge transport in the hole-transporting or the light-emitting layer could be limiting, by varying the thicknesses of the PTAA and the Alq_3:DCM_2 layers. Figure 5.2(b) shows the dependence of the light intensity on the pulse width for OLEDs comprising 15 nm or 50 nm PTAA, whereas in Fig. 5.2(c) the thickness of the active light-emitting layer was changed. Figure 5.2

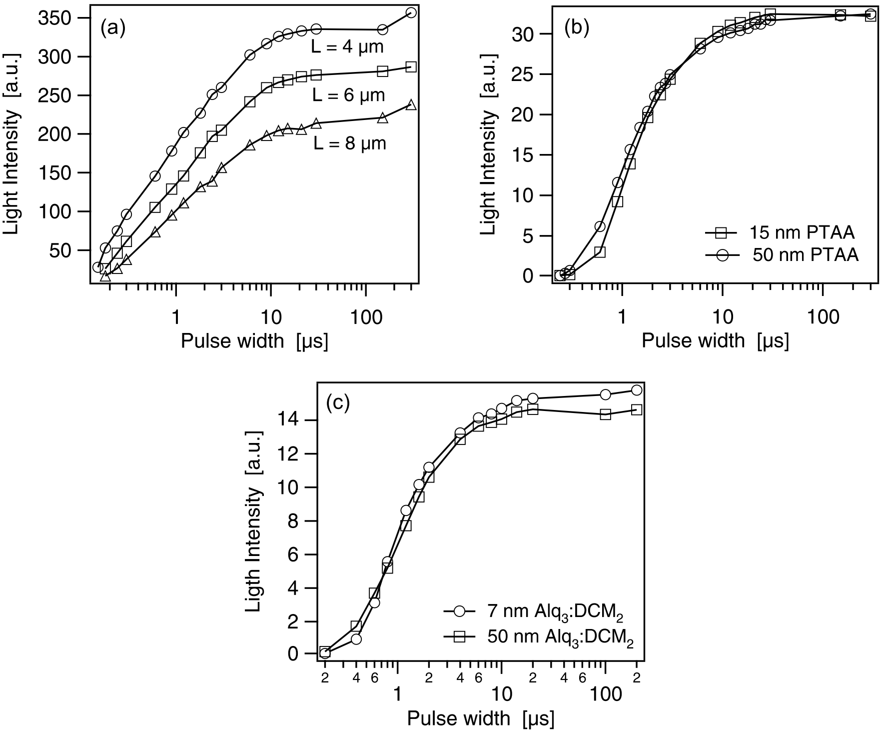


Fig. 5.2 Dependence of the peak light intensity on the pulse width for (**a**) OLEDs with field-effect-assisted electron transport with, respectively, a distance of 4 μm, 6 μm and 8 μm between the metallic contact and the insulator edge, (**b**) conventional OLEDs comprising 15 nm or 50 nm PTAA, and (**c**) conventional OLEDs having an active layer of 7 nm or 50 nm thick. The OLEDs with field-effect-assisted electron transport were biased at 20 V, whereas 7 V was applied to the conventional OLEDs. (© 2010 IEEE)

shows that the dependence of the light output on the applied pulse duration is invariant with the thickness of the layers, and hence not limited by the transit times of the charge carriers through the layers in our device structure.

Charge Accumulation

In multi-layer OLEDs, however, not only charge transport, but also charge accumulation at the hetero-interfaces between the different semiconductors should be taken into account [295]. The energy level diagram under flat band conditions, shown as inset in Fig. 5.1, clearly indicates the presence of energy level offsets at the organic/organic interfaces. Consequently, injected electrons and holes, transported through the PTCDI-$C_{13}H_{27}$ and PTAA layer, respectively, will accumulate at these interfaces before injection into the active light-emitting layer. Depending on the applied electric field, space charge will be built up faster and the charges will more

Fig. 5.3 Pulse-width dependence of a standard OLED comprising PTAA/Alq$_3$:DCM$_2$/PTCDI-C$_{13}$H$_{27}$ as the organic layer stack biased at different voltages. (© 2010 IEEE)

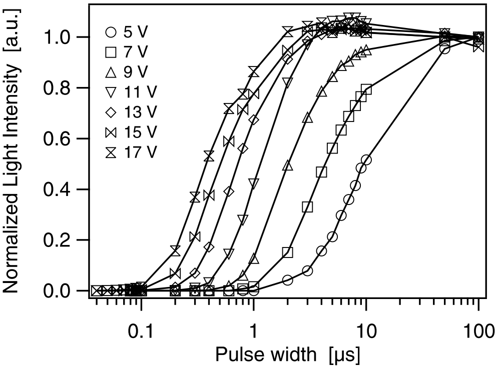
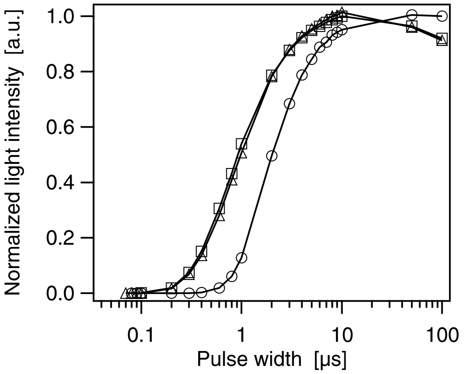


Fig. 5.4 Normalized light intensity as a function of the pulse width of OLEDs using: PTAA/Alq$_3$:DCM$_2$/PTCDI-C$_{13}$H$_{27}$ (*open circles*), PTAA/Alq$_3$:DCM$_2$ (*open triangles*), and PTAA/Alq$_3$:DCM$_2$/Alq$_3$ (*open squares*) as the organic layer stack. A bias of 9 V was applied to the devices. (© 2010 IEEE)



easily overcome the present energy barriers. The dependence of the light intensity on the pulse width for an OLED biased at different voltages is shown in Fig. 5.3. It can be clearly seen that the minimum allowable pulse width without reduction of the light intensity decreases from 10 µs to about 1 µs when higher voltages were applied. This points out that one of the organic/organic interfaces indeed limits the behavior of the device under pulsed excitation.

To verify which interface is the limiting factor two additional OLEDs were fabricated: ITO/PTAA/Alq$_3$:DCM$_2$/LiF/Al and ITO/PTAA/Alq$_3$:DCM$_2$/Alq$_3$/LiF/Al. In both devices the energy barrier between the electron-transporting layer and the active light-emitting layer is eliminated. The total thickness of the organic layers was kept constant in order to apply the same electric field over the devices. Consequently, the first device used 70 nm of Alq$_3$:DCM$_2$, whereas the second OLED had a 20-nm thick Alq$_3$:DCM$_2$ layer and 50 nm undoped Alq$_3$. Figure 5.4 compares the light output of these two OLEDs with the one of Fig. 5.3 as a function of the pulse width when a bias of 9 V is applied. A clear difference in pulsed excitation behavior is observed. The minimum pulse width that could be applied without affecting the light intensity shifted to shorter values when the energy offset at the interface between the PTCDI-C$_{13}$H$_{27}$ and the Alq$_3$:DCM$_2$ layer was eliminated. This indicates that it is the PTCDI-C$_{13}$H$_{27}$/Alq$_3$:DCM$_2$ interface that has a limiting effect on the pulsed excitation properties of our light-emitting devices. Since this interface is present in the conventional OLED as well as in the OLED with field-effect electron transport, it is obvious that the minimum allowable pulse width without reduction of the light intensity is similar for both devices (Fig. 5.1). The fact that the dependence on the pulse duration is weaker in the case of an OLED with field-effect-assisted electron transport can be understood by a spread in potential drop. Indeed, the light-emission zone of an OLED with remote cathode is approximately 2 μm wide (Sect. 3.3). Over this area the potential drop over the PTCDI-$C_{13}H_{27}$/Alq_3 interface decreases with the distance from the insulator edge. Therefore, an OLED with field-effect electron transport has to be interpreted as the sum of sections of standard OLED devices, each with a different voltage over the PTCDI-$C_{13}H_{27}$/Alq_3 hetero-interface. This indeed leads to an overall weaker dependence of the light intensity on the pulse duration, as observed in Fig. 5.1.

5.2 Triplet Excitation Scavenging in Films of Conjugated Polymers

The accumulation of triplets is a problem inherent to organic materials and is a well-known issue also in classical liquid-state organic dye lasers, using highly fluorescent organic dye molecules dissolved in organic solvents. Triplet-state losses often limit the lasing performance of these dye lasers, especially at CW operation [296]. Consequently, organic dye lasers normally operate in pulsed mode (pulse duration of several nanoseconds) using a short-pulse flash-lamp for pumping since only in this way the accumulation of dye molecules in the triplet state can be overcome. To allow long-pulse operation, so-called triplet scavengers are usually employed [297]. This is described in Sect. 5.2.1. The use of triplet scavengers in solid-state organic thin films is investigated in Sect. 5.2.2.

5.2.1 Triplet Scavenging in Liquid-State Organic Dye Lasers

To circumvent triplet accumulation, introducing severe triplet-triplet absorption at the expected fluorescent lasing wavelength, the commonly accepted practice in liquid-state organic dye lasers is to use triplet scavengers [297]. It was demonstrated that the accumulation of dye molecules in the triplet state can be reduced by adding such molecules to the dye solution [297–299]. In this way, quenching of lasing emission by triplets might almost be eliminated. To reduce triplet accumulation, the triplet scavenger molecule should meet some important requirements:

- It should have the ability to accept a triplet excitation from the dye molecules, implying that its triplet level should be low enough.
- At the same time its singlet level should be high enough to prevent quenching of singlet excitations of the dye molecules. This implies thus that the S_1-T_1 splitting for the triplet scavenger should be extraordinary large.

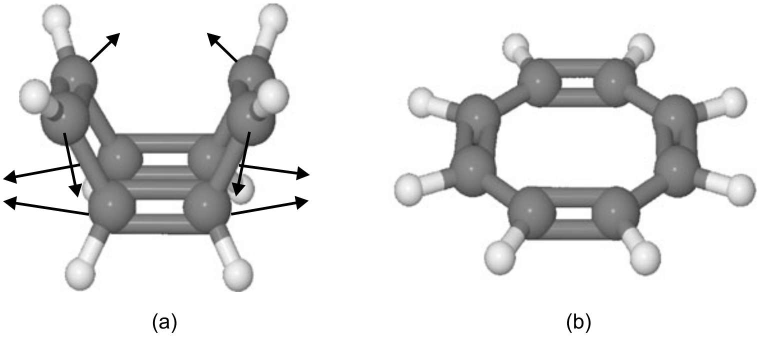


Fig. 5.5 (**a**) Illustration of the ground-state conformation of COT. The direction of the concerted C=C stretching and C–C torsional vibrations that planarize the molecule during triplet energy transfer are indicated by arrows. (**b**) The flat octagonal geometry of the COT triplet state

- It should possess a reasonably short intrinsic triplet lifetime to deplete quickly the triplet population or/and have intrinsic triplet-triplet absorption shifted far from the region of lasing of the dye molecules.
- It should not enhance intersystem crossing of the dye molecules to prevent converting singlets into triplet excitations. This criterion imposes a certain limitation for employing compounds containing heavy atoms (like metal-organic complexes) as triplet scavengers [300].

Taking into account all these requirements, it is not surprising that there are just a very limited number of efficient triplet scavengers available today.

The cyclic non-aromatic polyene, 1,3,5,7-cyclooctatetraene (COT), is the most popular and efficient triplet scavenger in liquid-state organic dye lasers due to its unique combination of properties, namely the ability to quench host triplets with an energy as small as 0.8 eV [301] and its very short triplet lifetime ($\sim$100 μs) [302]. The use of COT as an efficient triplet scavenger for several laser dye solutions is well documented [297–299], particularly, it was used commercially in Rhodamine-6G dye lasers to reduce excited triplet absorption. In addition, the mechanism for the energy-transfer process has been investigated in detail [301–303]. Unlike molecular oxygen, which is known as a notorious triplet quencher due to its triplet ground state, COT can quench triplets without increasing the intersystem crossing rate and without oxidation of the dye molecules. COT is a flexible molecule in the ground state and belongs to the "non-classical" triplet acceptors, which exhibit anomalous nonvertical (non-adiabatic) triplet energy transfer. The ground-state conformation of COT is illustrated in Fig. 5.5(a). During triplet energy transfer concerted C=C stretching and C–C torsional vibrations deform the molecule, favoring a more planar geometry as illustrated in Fig. 5.5(b) [301, 302].

Generally, an electronic transition is termed "vertical" with respect to the equilibrium geometry, conveying the idea that the electron is excited to the upper state before the nuclei have had the time to re-equilibrate. This is also known as an "adiabatic transition" [21]. It comes from the Franck-Condon principle (Sect. 1.1.3) according to which electronic transitions occur vertically since there is no change of the internuclear distance during the fast electron transition [20]. In other words, the nuclei are considered to be static with respect to the changes and movements of the electrons and the nuclear coordinates can be separated from the electronic part. It also implies that triplet energy transfer from a donor to an acceptor molecule normally is vertical, which means that the geometry of the molecule is not changing. This is true for organic molecules with rigid framework, which can be considered as "classical" triplet acceptors. For classical triplet acceptors the triplet energy transfer process depends mainly on the triplet energy of the molecule. This means that it is thermally activated in the case when the energy of the accepting molecule is higher than that of donor molecule (i.e. negative energy balance, $\Delta E_T < 0$) and that the activation energy is just the triplet energy difference [303].

"Nonvertical" transitions, on the other hand, imply a strong deformation of the acceptor molecule (also called "non-adiabatic transition") [304]. Non-vertical triplet energy transfer implies that the acceptor geometry changes concurrently with its excitation and therefore, it can only occur for some acceptor compounds, such as COT, cycloheptatriene [305], cis-stilbene, etc., which manifest significant flexibility. These molecules are also known as "non-classical" acceptors. In contrast to classical acceptors mentioned above, for nonvertical non-classical acceptors triplet energy transfer also depends on the molecule itself (its flexibility and geometrical distortion) and not only on its triplet energy [303]. Experimentally, nonvertical triplet acceptors exhibit a considerably faster triplet energy transfer rate in the regime of negative energy balance versus the vertical triplet energy (endothermic situation, $\Delta E_T < 0$), compared to the one predicted for a thermally activated Arrhenius process [304]. This is a consequence of the fact that nonvertical triplet energy transfer is accompanied by a geometrical distortion of the molecule, which results in a considerable lowering of the triplet state due to molecular relaxation. This relaxed triplet state of the nonvertical acceptor has considerably lower energy than that of the non-relaxed one. Consequently, nonvertical triplet acceptors can capture relatively low lying triplet excitations of donor molecules. The nonvertical acceptor COT, for example, can quench donor triplets with an energy ≥ 0.8 eV [301]. In addition, due to the relatively small energy distance between the relaxed triplet state and the ground state of such compounds, their triplet state possess a short lifetime as the probability of non-radiative energy dissipation increases exponentially with lowering the above energy difference [305].

5.2.2 Triplet Scavenging in Solid-State Organic Thin Films

Nonvertical triplet scavengers, such as COT, were so far only used in dye solutions and it is not obvious whether they can work in solid-state matrices as well. It is known that quenching of host triplets by COT requires a planarization of the COT molecule during triplet energy transfer [303, 305], otherwise the transition would be endothermic. In solution there are no steric restrictions for molecular deformation, however, it is not clear if such a structural reorganization could be hindered in a solid environment.

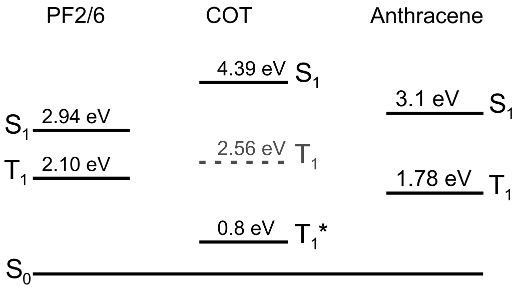


Fig. 5.6 Energy level scheme for PF2/6, COT and anthracene. The dashed line indicates the position of the T_1 triplet state of the COT molecule. This triplet state, however, is lowered during energy transfer due to molecular relaxation. The position of the relaxed triplet state of the COT molecule is indicated by T_1^*. (© Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)

Besides, the energy transfer mechanism in liquid solutions is different from that in a solid-state matrix where it is dominated by a short-range Dexter mechanism (Sect. 1.3.3). When molecules are separated in liquid diluted solution, they have to approach each other to sufficiently small distance via diffusion of acceptor and donor molecules in the liquid in order to form an "encounter complex" where the triplet energy transfer process can happen. When the balance between the energies of the donor and acceptor triplet states (ΔE_T) is positive, triplet energy transfer in liquid solutions is controlled by diffusion of molecules in the liquid medium. In the case of negative energy balance ($\Delta E_T < 0$), the triplet energy transfer rate is additionally affected by a thermally activated Arrhenius process where ΔE_T is the activation energy. On the other hand, in solid-state organic molecules cannot easily diffuse and therefore the above mentioned molecular diffusion mechanism is not operative. Instead, triplet excitations can move from molecule to molecule via Dexter energy transfer owing to sufficiently small intermolecular separation (typically less than 1 nm). In other words, triplet energy transfer in solid matrices is controlled by diffusion of triplet excitons rather than by diffusion of molecules.

The goal of the present study is to elucidate whether "non-classical" triplet scavengers, such as COT, used before in liquid-phase organic dye lasers can also be used to scavenge host triplet excitations in solid-state highly fluorescent organic semiconductors. In our study we investigate the use of COT in polymer films of the polyfluorene derivative PF2/6. Polyfluorene is a prospective material for the fabrication of thin-film organic lasers [99, 141], where accumulation of triplets under electrical pumping is a very important issue. We also compare these results with those obtained by using a "classical" triplet acceptor with rigid molecular framework (anthracene), which also possesses suitable energetic levels to scavenge polyfluorene host triplets. The structural formulas of these compounds can be found in Chap. 2 (Sect. 2.1.1); the position of their S_1 and T_1 energy level are displayed in Fig. 5.6.

It should be mentioned that conventional vertical triplet energy transfer has been well documented for solid films of conjugated semiconducting polymers such as PPV derivatives [306], polyfluorenenes and MeLPPP [307], however, to the best of our knowledge no nonvertical triplet energy transfer has been reported for them.

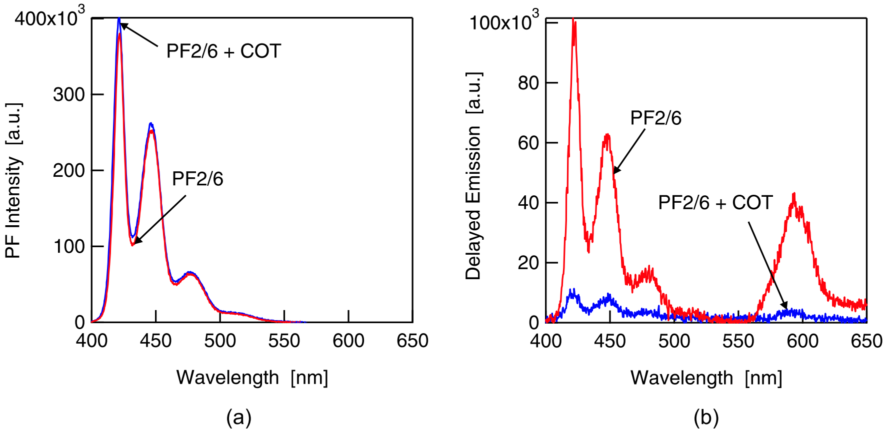


Fig. 5.7 (**a**) Prompt fluorescence intensity of a neat PF2/6 film and PF2/6 doped with 10 wt% COT registered at 77 K, and (**b**) Delayed emission spectra of the same films detected at 77 K at a time delay of 100 μs between the exciting laser pulse and the detection window. (© Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)

Triplet Scavenging by the Non-classical Triplet Acceptor COT

Polymer films doped with triplet scavenger molecules were prepared by dissolving COT and PF2/6 in a ratio 1/10 in THF[1], and then drop-casting the resulting solutions on a precleaned quartz substrate. To delay evaporation of the COT, which is liquid at room temperature, the films were dried in a saturated COT environment. In order to exclude the presence of molecular oxygen in the fabricated organic films, solutions were prepared in a N_2-filled glovebox using de-aerated solvents.

Figure 5.7(a) shows the spectra of the prompt fluorescence (PF) from a neat PF2/6 film and from a PF2/6 film doped with 10 wt% COT registered at 77 K during the laser pulse excitation. These spectra are coincident with the steady-state PL spectra of these films, implying that the fluorescence in the range of 420–550 nm, caused by the radiative decay of singlet excitons, is dominant in this material. This is in line with earlier observations [308]. Note that virtually the same fluorescence intensity was observed in neat and doped PF2/6 films suggesting that the COT dopant does not quench singlet excitons in these films.

The delayed emission spectra of the same neat PF2/6 film and PF2/6 film doped with COT detected by introducing a time delay ($t_{del} = 100$ μs) between the exciting laser pulse and the detection window of the registration system is depicted in Fig. 5.7(b). As expected, delayed emission of the PF2/6 film consists of two different components with different spectral position. The short wavelength component in the blue spectral region, which is virtually identical to the prompt fluorescence spectrum, is due to delayed fluorescence (DF) from the S_1 state of PF2/6, while the second longer-wavelengths spectral component at ~590 nm can only be seen

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[1] Tetrahydrofuran.

in the delayed emission and has been assigned to intrinsic phosphorescence (Ph) from the T_1 state [308]. It should be mentioned that, in contrast to very thin PF2/6 films (<100 nm) (not shown here), thicker drop-casted films normally do not exhibit vibronic fine structure of Ph spectra as could be seen from Fig. 5.7(b). This effect was explained before [308] in terms of somewhat different morphology of films of different thicknesses and agrees completely with the spectra reported earlier [308, 309]. Remarkable is that the intensity of the delayed emission from the neat and doped PF2/6 film was found to be drastically different, which is opposite to their prompt fluorescence (Fig. 5.7(a)). As can be seen on Fig. 5.7(b), both the DF and Ph are largely reduced in films doped with COT. This implies a strong quenching of the delayed emission in PF2/6 films by COT molecules, while at the same time the prompt fluorescence is not affected. This can be attributed to the extremely large singlet-triplet (S_1-T_1) splitting of the COT molecules (Fig. 5.6). The observed quenching effect is principally similar for different delay times.

A remarkable result of the present study is that it demonstrates that the non-classical triplet acceptor COT can be used as an efficient triplet scavenger also in a solid polymer film. Since during triplet energy transfer the COT molecule should be planarized [301–303, 305]—a process that can easily occur in liquid phase—the presented results suggest that such a structural reorganization seemingly is not hindered in a solid environment even at low temperature. In addition, the presented results prove that triplets' diffusion migration in the host PF2/6 polymer is sufficiently efficient even at low temperature. Therefore, triplets can be quenched similarly as in liquid solution, where triplet transfer occurs by dye-molecule colliding with the triplet scavenger.

Another important implication of this study is that it suggests that non-classical nonvertical triplet acceptors could be considered as a promising class of efficient triplet scavengers for solid-state electrically-pumped organic light-emitting devices due to (i) an exceptionally large energy splitting between the lowest excited singlet state (4.39 eV for COT) [302] and the relaxed triplet state, which is inherent for these compounds, and (ii) a reasonably short triplet lifetime ($\sim$100 μs for COT) that enables fast deactivation of triplet excitations. In this way, the accumulation of triplets, introducing triplet-state losses such as singlet-triplet annihilation and triplet-triplet absorption, might be considerably reduced.

Triplet Scavenging by the Classical Triplet Acceptor Anthracene

To compare the observed host triplet quenching effect in PF2/6 due to "non-classical" COT dopants with the effect of the presence of "classical" triplet scavengers, thin PF2/6 films doped with anthracene were prepared. The conventional aromatic molecule anthracene (energy levels shown in Fig. 5.6) has a very low triplet level (1.78 eV) [9] and an exceptionally large S_1-T_1 energy level splitting (1.32 eV) compared to other organic conjugated small molecules and was therefore chosen as triplet acceptor. Anthracene additives in PF2/6 films present thus an example of a classical triplet scavenger for which a vertical (adiabatic) triplet energy transfer

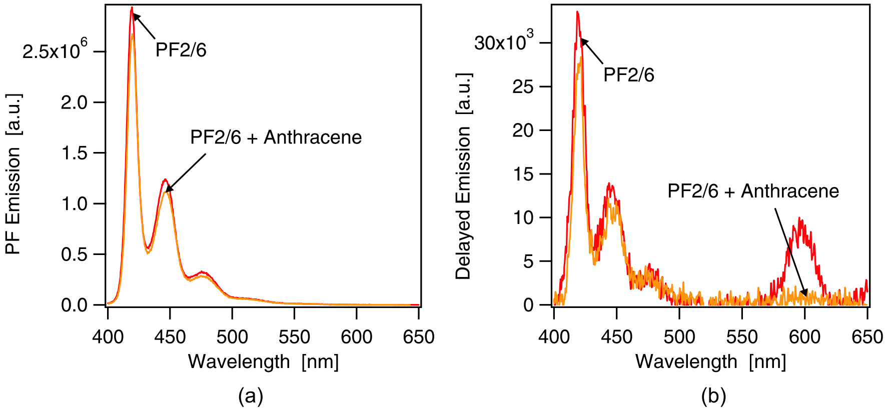

Fig. 5.8 (**a**) Prompt fluorescence, and (**b**) delayed emission spectra of a neat PF2/6 film and a PF2/6 film doped with 20 wt% anthracene. The spectra were measured at 77 K at a time delay of 100 µs. (© Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)

process is operative. Anthracene doped PF2/6 films were prepared by spin-coating a 20 wt% solution from toluene at 1000 rpm. Also here, solutions were prepared in a N_2-filled glovebox using de-aerated solvents in order to exclude the presence of molecular oxygen in the organic films. A comparison of the prompt fluorescence of the neat PF2/6 and PF2/6 film doped with anthracene at 77 K is presented in Fig. 5.8(a). Delayed emission spectra of these films ($t_{del} = 100$ µs) are shown in Fig. 5.8(b).

As can be seen from Fig. 5.8(b), anthracene dopants in PF2/6 films do quench host phosphorescence due to exothermic triplet energy transfer from the triplet state of the polymer ($E_T^{PF2/6} = 2.10$ eV) [308] to the one of anthracene ($E_T^{anthracene} =$ 1.78 eV) [9] and this quenching effect is not very different from the one observed with the non-classical COT triplet acceptor. Since the singlet state of anthracene (3.1 eV) [9] is higher than the one of PF2/6, it is natural that the prompt fluorescence intensity of the polymer is not quenched by the presence of anthracene additives (Fig. 5.8(a)).

Comparison of the delayed emission spectra of PF2/6 doped with COT and anthracene additives shows, however, that these triplet scavengers have very different effect on the delayed fluorescence (DF) of the PF2/6 polymer. As can be seen, while COT dopants strongly quench the DF of the PF2/6 (Fig. 5.7(b)), anthracene doping has almost no effect on the host DF (Fig. 5.8(b)).

To rationalize these observations one should consider the origin of the DF in PF2/6 polymer films. Previous time-resolved PL studies [308] reveal that the DF emission in PF2/6 polymer films is dominated by triplet-triplet annihilation. Triplet-triplet annihilation arises due to a bimolecular reaction between two triplet excitations ($T_1 + T_1 \rightarrow S^* + S_0$) and therefore, the DF intensity should be a quadratic of the triplet concentration. Our measurements support such a notion as indeed the DF intensity in the PF2/6 film was found to increase quadratically with the excitation intensity within the considered laser intensity range. This is illustrated in Fig. 5.9(a),

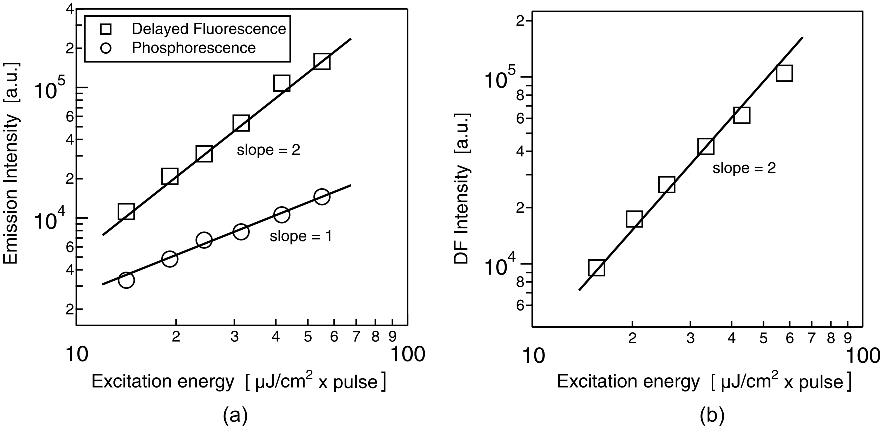

Fig. 5.9 Intensity dependence upon laser excitation intensity of (**a**) the DF and Ph emission in neat PF2/6 films, and (**b**) the DF emission in PF2/6 films doped with anthracene. (© Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission)

which shows the intensity dependence of the DF and Ph emissions in neat PF2/6 films upon the laser excitation intensity. To have the maximum signal possible, the delayed emission spectra were recorded with a time delay of 75 ns and a gate width of 10 ms, i.e. in integration mode. The emission intensities plotted in Fig. 5.9(a) are the peak emission intensities (0-0 peak for the DF). The quadratical increase of the DF intensity upon laser excitation clearly points to a bimolecular origin of the DF emission (DF $\sim I_{exc}^2$). At the same time the phosphorescence intensity of the polymer increases linearly with the pumping intensity (Ph $\sim I_{exc}$), implying that the DF is quadratically proportional to the triplet concentration in the film.

Reduction of the DF intensity in PF2/6 films doped with COT can be readily explained by the fact that the COT molecules capture host triplets and deactivate them within the relatively short lifetime of the COT triplet state ($\sim$100 μs), thus preventing their possible annihilation. Anthracene additives in PF2/6 films also capture host triplets efficiently as evidenced by a strong reduction of the host phosphorescence (Fig. 5.8(b)); however, due to the very large radiative lifetime of the anthracene triplet state ($>$10 ms) [9] triplets are not deactivated quickly, but rather accumulated on the anthracene molecules. The results above clearly indicate that in order to control the triplet concentration efficiently, a suitable triplet scavenger should not only possess a sufficiently large S_1-T_1 energy level splitting, but should also have a reasonably short triplet lifetime, making a fast deactivation of triplet excitations possible. Anthracene additives are therefore not useful to reduce the triplet concentration. They may scavenge host triplet excitations, but due to their long triplet lifetime an accumulation instead of a reduction of the triplet population will occur.

Furthermore, the DF emission in PF2/6 films doped with anthracene was found to originate also from a bimolecular process in the host-guest system since the DF intensity increases quadratically with the excitation intensity as can be seen from Fig. 5.9(b). Since the host triplets are eventually transferred to the anthracene guest, as proven by strong quenching of the intrinsic PF2/6 phosphorescence (Fig. 5.8(b)), T_{host}-T_{host} annihilation cannot be responsible for the observed DF. On the other hand, T_{guest}-T_{guest} annihilation is also unlikely to be a dominant mechanism for the DF owing to the dopant dilution in the polymer host that precludes short-range Dexter-type triplet migration via the guest manifold. We therefore assume that the observed bimolecular annihilation proceeds via a T_{guest}-T_{host} annihilation reaction, i.e., when a mobile host triplet encounters a long-lived localized guest triplet excitation on an anthracene molecule, although clarifying this issue requires further investigations.

It has to be noticed that a similar mechanism was suggested before to explain DF in some conjugated polymers doped with metal-organic complexes [310, 311]. During such a T_{guest}-T_{host} annihilation process the excited singlet state of either the host or the guest molecule can be populated with equal probability, but since the host singlet state is lower than the singlet state of the anthracene dopant, only DF fluorescence of the PF2/6 polymer is observed.

5.3 Summary and Conclusions

In this chapter, two different approaches to reduce the triplet concentration in organic light-emitting devices were investigated. First, the pulsed excitation behavior of OLEDs with field-effect-assisted electron transport was discussed and their performance was compared to conventional OLEDs using the same organic layers. We found that not charge carrier transport, but injection of electrons from the electron-transporting layer into the active light-emitting layer determines the dependence of the light intensity on the applied pulse width. Since this interface is present in conventional OLEDs as well as in OLEDs with field-effect electron transport, similar pulse-width dependence was observed for both devices. Furthermore, we proved that, depending on the applied voltage and for this particular material combination, pulses down to 1 μs could be applied without affecting the light intensity. This fact is important for the control of the triplet concentration. 1 μs is much shorter than the typical triplet lifetime of fluorescent materials, indicating that pulsed excitation could be applied to reduce triplet accumulation in our device.

An alternative way to reduce the triplet concentration is the incorporation of a triplet scavenger, as discussed in the second part of this chapter. Phosphorescence and delayed fluorescence of polyfluorene polymer films doped with cyclooctatetraene (COT) and anthracene were investigated by time-resolved photoluminescence measurements. Using the “non classical” triplet scavenger COT, employed before in liquid-phase organic dye lasers, anomalous nonvertical triplet energy transfer in solid conjugated polymer films was demonstrated for the first time. This triplet energy transfer behaves similarly to the one of vertical triplet acceptors like anthracene. Thanks to their large singlet-triplet splitting, both dopant molecules were found to quench efficiently host phosphorescence without affecting the host fluorescence. This S_1-T_1 energy level splitting is exceptionally large in COT due to its low-lying relaxed triplet state capable of accepting host triplet excitations. In addition, contrary to anthracene, the triplet lifetime of COT molecules is reasonably short, making a fast deactivation of triplet excitations possible. This suggests that nonvertical triplet scavengers, which possess a large S_1-T_1 energy level splitting and an inherently short lifetime of their relaxed triplet state, could be promising candidates for quenching host triplet excitations in electrically pumped organic lasers and other high-brightness organic light sources.