

Triplet Harvesting and Singlet Harvesting

In an electro-luminescence process, the population of excited states occurs via a recombination of negatively charged electrons and positively charged holes. They attract each other by Coulomb interaction (Figure 1a) and form excitons in the emission layer of an OLED. Since both, hole and electron, have spins, four different spin combinations are possible. According to quantum mechanics (compare for example [1-3]), *one* combination of antiparallel spins, giving a singlet, and *three* combinations of parallel spins, giving a triplet, occur. (Figure 1b) Thus, in a statistical limit, 25 % of the excitons represent singlets and 75 % triplets.

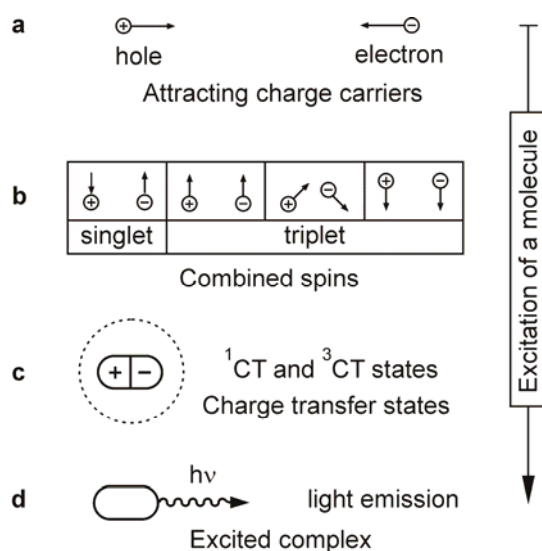


Figure 1. Schematic description of (a) electron-hole recombination, (b) spin combinations, giving one singlet state and one triplet state. (c) The process of population of the lowest excited states proceeds via singlet and triplet charge transfer (CT) states which involve the emitter and surrounding host molecules. (d) From these CT states relaxations populate the lowest excited states of the emitter [4,5].

In suitable situations, a single charge carrier is trapped first on the emitter complex, oxidizing or reducing it. For example, for OLEDs employing several Ir(III) complexes, the hole is trapped first [6]. Subsequently, the electron is attracted and the exciton is formed. The processes of population of an excited state of the emitter complex can be described to proceed via singlet (¹CT) and triplet (³CT) charge transfer states, as proposed by Yersin [4,5]. These involve the emitter complex and the immediate environment, which usually consists of

organic host (matrix) molecules. (Figure 1c) Because of the small SOC constants of the host molecules and the very small energy splitting between the ^1CT and ^3CT states, it is expected that the intersystem crossing (ISC) time between these two states is significantly longer than relaxation times to lower lying states with the same multiplicity (internal conversion, IC). These latter processes take place in about 10^{-12}s [2]. Therefore, fast and separate relaxations without spin flips are expected to populate the lowest excited singlet state S_1 (one path) and the triplet state T_1 (three paths) of the emitter complex, respectively. (Figure 1d) Subsequently, ISC from the S_1 to the T_1 state can occur.

Based on these model considerations, we can now explain the distinct differences between organic and organo-transition metal emitters for OLED applications. The corresponding processes are schematically displayed in Figure 2. After the exciton is formed and the relaxations by one singlet and three triplet paths have occurred, the lowest excited singlet and triplet states are populated. This is valid for organic as well as for organo-transition-metal emitter materials. The corresponding processes are schematically displayed in Figure 2b. The organic molecule can exhibit an efficient and fast decaying singlet emission ($S_1 \rightarrow S_0$) with lifetimes τ of the order of 1 to 100 ns with a fluorescence quantum yield of almost 100 % [7-9], if the $S_1 \rightarrow T_1$ intersystem crossing rate is small compared to the fluorescence rate. For organic molecules with $^{1,3}\pi\pi^*$ states, for example, ISC times can be as long as 0.1 to 1 μs [2]. On the other hand, since the probability for the radiative $T_1 \rightarrow S_0$ transition is also very small, the deactivation of the T_1 state occurs normally non-radiatively at ambient temperature. Therefore, 75 % of the excitons, namely the triplet excitons, are lost for the emission. Their energy is transferred into heat. (Figure 2a) The conditions are more favorable for organo-transition metal complexes, in which the central metal ion induces significant spin-orbit coupling (Figure 2c). For these complexes, ISC to the lowest T_1 state is usually very efficient and thus, at an energy separation between the S_1 and T_1 states of several 10^3 cm^{-1} , a singlet S_1 emission is not observable. Moreover, the radiative $T_1 \rightarrow S_0$ rate can become relatively large for compounds with central metal ions with large SOC constants so that efficient phosphorescence with a quantum yield of almost 100% can occur even at ambient temperature [10-12]. Consequently, all four possible spin orientations of the excitons can be harvested to populate the lowest T_1 state. By this process of *triplet harvesting* one can, in principle, obtain a four times higher electro-luminescence efficiency with phosphorescent triplet emitters than with fluorescent singlet emitters.

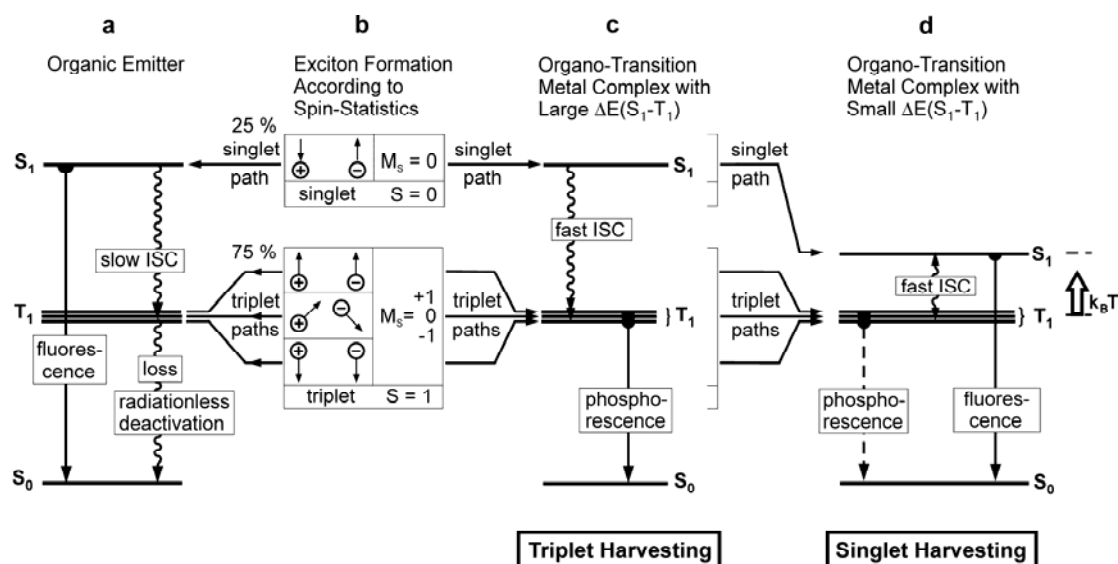


Figure 2. The diagram displays electro-luminescence excitation processes for organic and organo-transition metal emitters, respectively, and explains triplet harvesting and singlet harvesting. (b) Due to spin-statistics, electron-hole recombination leads to 25% singlet and 75% triplet state population. (a) In organic molecules, only singlets emit light (fluorescence), while the triplet excitation energy is transferred into heat. (c) Organometallic compounds with transition metal centers show a fast intersystem crossing (ISC) from the singlet state S_1 to the lowest triplet state T_1 . Thus, this triplet state *harvests* singlet and triplet excitation energy and can efficiently emit [4,5]. (d) For complexes with small energy separations of $\Delta E(S_1-T_1)$ fast up and down ISC processes can occur, which can lead to an efficient thermally activated fluorescence. (Compare section 9.) Also in this case, all singlet and triplet excitons are harvested, but the emission represents a short-lived, thermally activated $S_1 \rightarrow S_0$ fluorescence [13-18].

For several compounds, in particular for a number of Ir(III) complexes, the average radiative decay rate k_{av}^r of all three triplet substates is relatively large. For example, for Ir(ppy)₃ doped into PMMA, a value of $k_{av}^r \approx 6.9 \times 10^5 \text{ s}^{-1}$ ($\tau_{av}^r = 1.4 \text{ } \mu\text{s}$) has been found at ambient temperature [12]. Such high values are well suited for OLED applications by taking advantage of the triplet harvesting effect.

However, many other organo-transition metal compounds exhibit much lower average radiative rates for the $T_1 \rightarrow S_0$ transition. In this situation, the emission decay times are relatively long, if non-radiative processes do not lead to quenching. In this case, saturation

and/or triplet-triplet annihilation effects make these materials disadvantageous for OLED applications, as will further be discussed below. Interestingly, a new electro-luminescence mechanism, as recently proposed by Yersin et al [13-18], can overcome these problems in suitable situations. For these cases specific emitter materials are required. In particular, they should exhibit small energy separations $\Delta E(S_1-T_1)$ between the lowest excited singlet state S_1 and the triplet state T_1 (small exchange interaction integral) and should show an efficient thermally activated delayed fluorescence, an effect which has already been well known for a long time [2, 19-23]. Figure 2d displays this situation. After exciton formation in an emission layer of an OLED, one singlet path and three triplet paths populate both the S_1 and the T_1 state, respectively, similarly as described above. Again, induced by SOC, the ISC processes downwards from S_1 to T_1 are fast. However, due to the small energy separation $\Delta E(S_1-T_1)$, also upward processes from T_1 to S_1 are effective at ambient temperature. Thus, emission of both states can occur. As a result, the emission is governed by a Boltzmann distribution according to Eq. (1):

$$\frac{Int(S_1 \rightarrow S_0)}{Int(T_1 \rightarrow S_0)} = \frac{k^r(S_1 \rightarrow S_0)}{k^r(T_1 \rightarrow S_0)} \cdot \exp\left(-\frac{\Delta E(S_1-T_1)}{k_B T}\right)$$

(1)

Herein $Int(S_1 \rightarrow S_0)$ and $Int(T_1 \rightarrow S_0)$, $k^r(S_1 \rightarrow S_0)$ and $k^r(T_1 \rightarrow S_0)$ represent the fluorescence and phosphorescence intensities and the corresponding radiative rates, respectively. k_B is the Boltzmann constant and T the absolute temperature.

A numerical example may illustrate the advantage of this mechanism. Cu(I) complexes typically exhibit triplet emission decay times $\tau(T_1 \rightarrow S_0)$ of the order of 100 μ s up to a few ms [24-26]. An emitter with such a long decay time, e.g. of 1 ms, would not be suited for OLED applications. However, at an energy separation of, for example, $\Delta E(S_1-T_1) = 500 \text{ cm}^{-1}$ and a ratio of radiative rate constants of $k^r(S_1 \rightarrow S_0) / k^r(T_1 \rightarrow S_0) = 10^4$, the intensity of the $S_1 \rightarrow S_0$ fluorescence at ambient temperature is by a factor of the order of 10^3 stronger than the intensity of the $T_1 \rightarrow S_0$ phosphorescence, according to Eq. (1). Under the same conditions, the measured emission decay time, i.e. the averaged decay time of the two states S_1 and T_1 , is reduced from 1 ms to about 1 μ s. This decay time is attractively short and is similar to the value as found for Ir(ppy)₃.

In conclusion, singlet emitters in OLEDs that take advantage of the *singlet harvesting effect* by gathering both the triplet excitations (induced by three triplet paths) *and* the singlet excitation (effected by one singlet path) *and* by emitting a thermally activated fluorescence, might be similarly well suited for OLED applications as the already well established triplet emitter materials. In Ref. 27, we will discuss a promising material in some detail.

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