Drift-diffusion simulations of thermally activated delayed fluorescence OLEDs

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***Abstract*—In this work we present drift-diffusion simulations of a blue-emitting thermally activated delayed fluorescence (TADF) OLED. We exploited the ability of the multi-particle drift-diffusion model to explicitly calculate the charge transport for the different sub-populations in the TADF emitter, including singlet and triplet exciton states. The inclusion of proper models for the band-to-band transitions, for bimolecular recombination mechanisms and for inter-system crossing allows to investigate the device operation under different conditions. Moreover, it provides insight into the role of triplet-triplet annihilation and triplet-polaron quenching for the roll-off in internal quantum efficiency, which typically occurs in TADF OLEDs.**

I. Introduction

To date, organic light emitting diodes (OLEDs) represent the most promising and attractive technology for full-colour displays and lighting application. Their success is due to important features like large emitting area, ultra thin and flexible substrate compatibility, high colour quality and contrast ratio at low power consumption. For efficient OLEDs at least three important performance measures have to be guaranteed: (i) low operation voltage, (ii) high internal quantum efficiency (IQE) and (iii) high light extraction efficiency (LEE). Since the first OLED fabrication by Tang and Van Slyke[1], over the years, the research has been focused on the device design and performance improvement. In first-generation OLEDs based on fluorescent emitters the ideal IQE was 25% due to the limitation imposed by spin statistics leading to a singlet to triplet ratio of 1:3. Second-generation OLEDs based on phosphorescent emitters, instead, could ideally reach an IQE of 100% by exploiting the high spin-orbit coupling (SOC) due to the inclusion of organometallic complexes.

The use of the RGB technology in OLED displays makes the the blue emitter design definitely the most significant issue, because it requires wide bandgaps and typically exhibits limited lifetime stability problems[2]. In 2012, Uoyama et al.[3] demonstrated that the use of thermally activated delayed fluorescence (TADF) materials can successfully overcome these limitations. TADF OLEDs require a energy difference ΔE_{ST} between singlets and triplets in the fluorescent material of less than 100 meV, and can ideally harvest both singlets (S) and triplets (T) allowing an IQE of 100% and an external quantum efficiency (EQE) of nearly 20%. Under long triplet decay lifetime condition, a reverse inter-system crossing (RISC) mechanisms takes place in TADF materials, promoting T into S states. As a result, the radiative emission will be fostered by delayed fluorescence in addition to the prompt emission. Given the complexity of mechanisms involved, a versatile and fast simulation tool is crucial for device design and optimization.

II. The multi-particle drift-diffusion model

We use a multi-particle drift-diffusion model (mp-DD)[4] capable to calculate carrier transport explicitly accounting for both charged carriers and excitons. The model is based on the coupling of Poisson (1a) and transport equations (1b), and allows to define any number of carriers, each one with its own properties as charge, spin and density of states (DOS).

$$\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla \varphi) = -q \sum_i z_i n_i + qC \tag{1a}$$

$$\nabla \cdot (\mu_i n_i \nabla \phi_i) = R_i \ , \ \forall i. \tag{1b}$$

Each carrier population n_i is individually assumed in a local thermal equilibrium so that local quasi-Fermi levels ϕ_i can be defined. The transitions between populations, which are implemented as recombination-generation terms (R_i), is formulated in a strictly thermodynamically consistent way. The full system is discretized with a finite element method (FEM) and solved by the Newton method, as implemented in TiberCAD simulation tool.

III. Results and Discussion

In order to model the blue TADF OLED we perform DD simulations on the structure as shown in Figure 1, where the emitter (EML) consists of a host-guest blend with ratio 80:20. Simulations explicitly account for electron and hole sub-populations, and for exciton states in the EML. Here, we use for the exciton energies E_S^g = 2.56 eV and E_T^g = 2.49 eV on the guest material, and E_T^h = 2.84 eV on the host. Notably, the resulting ΔE_{ST} of 70 meV on the guest materil guarantees the the activation of the TADF mechanism. To describe the electron and hole transport bands (LUMO and HOMO) of the organic materials we use Gaussian density of states.

The exciton generation is controlled by rate constants of 10^{-31} cm^{3}s^{-1} and 10^{-30} cm^{3}s^{-1}, respectively in the host and guest material. according to experimental data, we set non-radiative and radiative exciton decay lifetimes to 5×10^{-5} s^{-1} and 1×10^{-8} s^{-1}. Simulations performed are aimed to investigate the IQE roll-off, which typically takes place at high current density[5]. To do this, we include in the model charge

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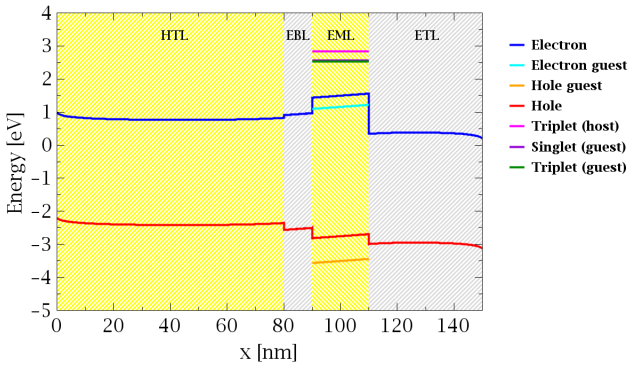

Fig. 1. LUMO and HOMO of carrier sub-populations, and average exciton state energy levels included in the TADF OLED system simulated.

transfer between HOMO and LUMO levels in EML, and the RISC between exciton states in the guest as

$$R_{nn^*} = C_{nn^*} n \left(1 - \frac{n^*}{N^*}\right) \left[1 - \exp\left(\frac{E_{f,n^*} - E_{f,n}}{k_B T}\right)\right] \tag{2a}$$

$$R_{ISC} = C_{ISC} n_S \left(1 + \frac{n_T}{N_T}\right) \left[1 - \exp\left(\frac{E_{f,T} - E_{f,S}}{k_B T}\right)\right]. \tag{2b}$$

Equation (2a) models the charge transfer between the host-guest system energy levels, taking into account the different electrochemical potentials ($E_{f,n}$ and E_{f,n^*}) and available states N^*. Equation (2b) models the ISC, where the direction (direct or reverse) depends on the difference between $E_{f,T}$ and $E_{f,S}$. We estimate the RISC contribution to the internal radiative emission in the EML, simulating the device once with C_{ISC}=10^{-13} cm^{3}s^{-1} and once neglecting ISC.

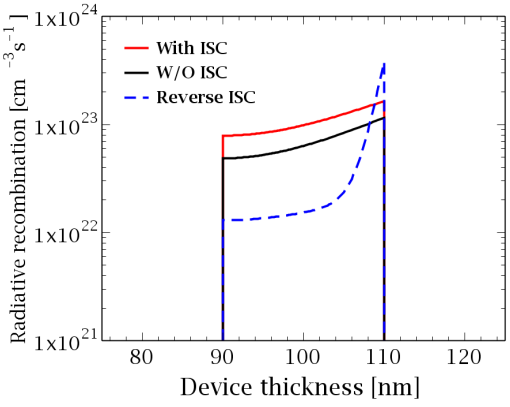

Fig. 2. Radiative emission profile either accounting and not the ISC (dashed-blue) at 6 V operation.

Figure 2 shows that the RISC increases the average radiative emission of 65%, with a peak contribution at EML/ETL interface where $E_{f,T} - E_{f,S}$ is significantly reduced. In addition, we observe that the mp-DD model is capable to calculate the radiative emission profile taking into account the different charge carrier injection from EBL/EML and EML/ETL interfaces. By including the most important recombination processes that affect the luminescent efficiency, such as triplet-triplet annihilation (TTA)[5] and triplet-polaron quenching (TPQ)[6], we estimated the IQE at different current densities.

$$R_{TTA} = C_{TTA} n_T^2 \left[1 - \exp\left(-\frac{2E_{f,T}}{k_B T}\right)\right] \tag{3a}$$

$$R_{TPQ} = C_{TPQ} n_T n_Q \left[1 - \exp\left(-\frac{E_{f,T}}{k_B T}\right)\right]. \tag{3b}$$

Equation (3a) models the interaction between two triplets ($n_T{}^2$) leading to the loss of one of them, while Eq. (3b) models a triplet recombining in presence of a polaron quencher, e.g. holes.

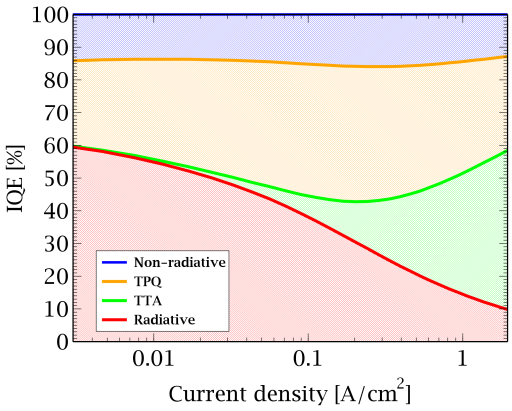

Fig. 3. Quantum efficiency contributions from non-radiative recombination, TPQ, TTA and internal radiative emission at different current densities.

In Figure 2 we report the contributions of the different loss mechanisms to the quantum efficiency, calculated at different driving currents. According to experimental observations in TADF OLEDs[5], TTA losses determine the IQE roll-off at high current densities. This effect is due to the increasing triplet density at high current densities, which reduces the triplet-to-singlet recycling that normally occurs via RISC.

References

[1] C. Tang and S. VanSlyke, "Organic electroluminescent diodes," *Appl. Phys. Lett.*, vol. 51, p. 913, 1987.

[2] X. Yang, X. Xu, and G. Zhou, "Recent advances of the emitters for high performance deep-blue organic light-emitting diodes," *Journal of Materials Chemistry C*, vol. 3, no. 5, pp. 913–944, 2015.

[3] H. Uoyama, K. Goushi, K. Shizu, H. Nomura, and C. Adachi, "Highly efficient organic light-emitting diodes from delayed fluorescence," *Nature*, vol. 492, no. 7428, p. 234, 2012.

[4] D. Rossi, F. L. Santoni, M. Auf der Maur, and A. Di Carlo, "A multi-particle drift-diffusion model and its application to organic and inorganic electronic device simulation," *submitted on IEEE Trans. Electron Devices*, 2019.

[5] K. Masui, H. Nakanotani, and C. Adachi, "Analysis of exciton annihilation in high-efficiency sky-blue organic light-emitting diodes with thermally activated delayed fluorescence," *Organic Electronics*, vol. 14, no. 11, pp. 2721–2726, 2013.

[6] R. Coehoorn, L. Zhang, P. Bobbert, and H. Van Eersel, "Effect of polaron diffusion on exciton-polaron quenching in disordered organic semiconductors," *Physical Review B*, vol. 95, no. 13, p. 134202, 2017.