Rational Materials Design Towards Singlet-Only Fluorescent OLEDs: Overcoming Traditional Spin Statistics

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Abstract

Efficient and durable deep blue emitters remain a critical bottleneck in OLED technology. Current approaches, such as triplet-triplet-fusion, thermally activated delayed fluorescence, hyperfluorescence, and phosphorescent systems, struggle with limited efficiency, stability issues, complex layer requirements, or limited industrial viability, primarily due to the persistence of harmful long-lived triplet states. We present a Singlet-Only emission system that promises to circumvent these challenges by leveraging an energetic resonance condition to bypass spin statistics, efficiently mitigating triplet formation. This enables the generation of nearly 100 % singlets on simple fluorescent emitters and offers a promising pathway to advance the performance and longevity of blue OLED devices.

Author Keywords

OLED; Efficient Blue; multiscale simulation; virtual microscope; virtual design; digital twin; emitter; host

1. Introduction

OLED displays have become commercialized but still fall short of expectations due to performance losses at high brightness levels and the aging of blue pixels in particular. For industrial applications, blue pixels require more complex layer structures and must be operated at reduced brightness, leading to increased power consumption, higher material and production costs, and limitations in OLED applications.(1)

A fundamental challenge in OLED operation is the presence of long-lived excited states (triplets), which, unlike the desired singlet states that quickly decay via light emission, may cause pixel degradation.(2) Approaches such as TADF and co-emission/hyperfluorescence have been explored to convert triplets into singlets, but they often require complex layer structures, precise alignment of multiple emitters and hosts, and are prone to stability issues, limiting their industrial viability.(3–5) Phosphorescent blue OLEDs, which harness radiative decay of triplet states, have also been extensively investigated but have yet to meet industrial performance and durability standards.(1,6) Despite substantial investments in the multi-million USD range, the development of efficient and durable blue OLED pixels remains an unresolved challenge, regarded as the holy grail of the display industry.(7,8)

Based on multiscale materials simulations,(9–15) we developed a Singlet-Only emission system that not only reduces but entirely circumvents the fundamental issues of OLEDs: By leveraging an energetic resonance condition between host and emitter material, spin statistics can be bypassed to generate nearly 100 % rapidly radiative singlets on regular fluorescent emitters. Harmful, long-lived triplets, which are inherent to conventional OLED emission systems, are effectively suppressed. Through an integrated approach combining computational simulations with experimental validation, we can efficiently design the required materials with short development cycles, aiming to achieve efficient and durable blue pixels.

2. The Singlet-Only approach

When a hole and an electron recombine to excitons in OLEDs, spin statistics dictate the generation of 75 % triplets and 25 % singlets. In classical fluorescent emission systems, i.e. a fluorescent emitter embedded in a host material, only the 25 % singlets can undergo radiative decay while 75% of the excitons are lost via thermal decay or in quenching processes, resulting in excess energy that can cause harm to the system and thereby lead to degradation of OLED devices.

For phosphorescent emission, the use of heavy metals in metal-organic complexes enhances the coupling between singlet and triplet states. Singlets transition almost instantaneously into triplet states, leading to 100% triplets, which couple to the radiation field via the singlet state and can decay radiatively. However, radiative decay time is 2–3 orders of magnitude slower than that of direct singlet radiative decay (fluorescence), resulting in long-lived excitons with increased risk of quenching in the system. While blue phosphorescent OLEDs remain an active area of research, the required lifetimes have not yet been achieved (16).

In thermally activated delayed fluorescence (TADF), triplets are converted into singlets to then decay radiatively. (17). This enables the utilization of 100% of the generated excitons. However, reducing the energy gap between the singlet and triplet states ("S-T gap") typically results in an increase in the radiative decay time of the singlets. Consequently, even within this approach, the radiative decay time is on the order of 10^{-6} seconds, leading again to the presence of long-lived excitons.(18)

In hyperfluorescent systems or co-emission, triplets generated on a phosphorescent or TADF emitter (A) are converted into singlets on a second fluorescent emitter (B), where they decay radiatively. As the energy transfer from A to B occurs up to an order of magnitude faster than the radiative decay of triplets on A, there are no long-lived triplets, and quantum yields of up to 100% can be achieved. However, the challenges of hyperfluorescence include the high complexity due to the use of two emitter materials, charge carrier trapping, and the potential trapping of long-lived triplets on the fluorescent emitter. (5,19,20)

In triplet-triplet fusion OLEDs (TTF) two low-energy triplets on neighboring molecules fuse into a singlet, which then decays radiatively. TTF has proven to be a promising strategy for singlet emission, even in the blue spectral range, but with the trade-off of larger pixels operated at reduced brightness, as the internal quantum efficiency (IQE) is inherently limited to a theoretical maximum of 62.5%.(20–24)

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In contrast to the above approaches, in an optimal Singlet-Only emission system, no triplets are formed at all. To realize Singlet-Only we have found a process (not to be disclosed here), where a resonance condition suppresses the formation of triplets and favors formation of singlets on fluorescent emitters. This effect has been observed in organic electronic systems, but is commonly overlooked in OLEDs. To exploit this effect, Singlet-Only emitters must satisfy three constraints of which two are related to their intrinsic energetics. Finally, to efficiently exploit this effect, the emitter needs to be carefully aligned energetically with the host material(s). In the following, we present intermediate results towards the development of Singlet-Only emission systems aiming at close to 100% singlet formation for the design of highly efficient and stable blue OLEDs.

3. Results

Parametric device simulations: To demonstrate the fundamental principle behind the Singlet-Only approach we conducted kinetic Monte-Carlo (kMC) simulations (25–27) to track the propagation of charges and excitons in an emissive layer (EML) consisting of an emitter material embedded into a single host material. For these fictitious materials, properties such as excitation energies, HOMO and LUMO energies, electronic couplings, etc. were set in a realistic range for prototypical materials of the respective type. We conducted simulations of three systems which only differed in the emitters used in EML: (i) a typical phosphorescent emitter (ii) a typical fluorescent emitter and (iii) a fictional fluorescent emitter that fulfills the Singlet-Only criteria and is well aligned with the host-material. Fig. 1a shows the roll-off of the internal quantum efficiency (IQE) over current density, for all three devices. The Singlet-Only device achieves close to 100 % IQE at low currents, compared to lower IQEs of approx. 71 % and 32 % for regular phosphorescent and fluorescent devices, respectively. Note that these devices were not optimized for the individual cases to allow a clean comparison of emitter performance. In Fig. 1b and 1c exciton life cycles of system (ii) and system (iii) are presented, i.e. the processes excitons undergo in the system starting with their creation as either singlets or triplets in the innermost circle. The fluorescent device with a standard emitter exhibits regular spin statistics: only 25 % of the excitons are generated as singlets, and 75 % as triplets that mostly undergo either thermal decay or polaron quenching (move_chg) with a small fraction of TTF processes. In contrast, all excitons in the Singlet-Only setup are singlets which can decay radiatively with only a small ratio being quenched by singlet-polaron quenching (SPQ).

We stress that the suppression of triplet formation is a direct effect of only the modification of material properties from system (ii) to system (iii). This demonstrates that by choosing an emitter with suitable properties together with a matching host material, formation of triplets can be suppressed by close to 100%.

Ab-initio simulations and experimental studies: From a dataset of 150000 molecules with computed excitation energies, we identified two suitable emitter candidates that satisfy the conditions for singlet only formation.To select host materials we did refined calculations on a dataset of 2400 molecules with excitation energies as well as HOMO and LUMO levels computed with the Nanomatch multiscale simulation workflow (9–15). We chose one of the structures, labeled so-zim-1, to realize a physical prototype. We note that while blue emission remains the ultimate target, this molecule does not emit in the deep blue range.

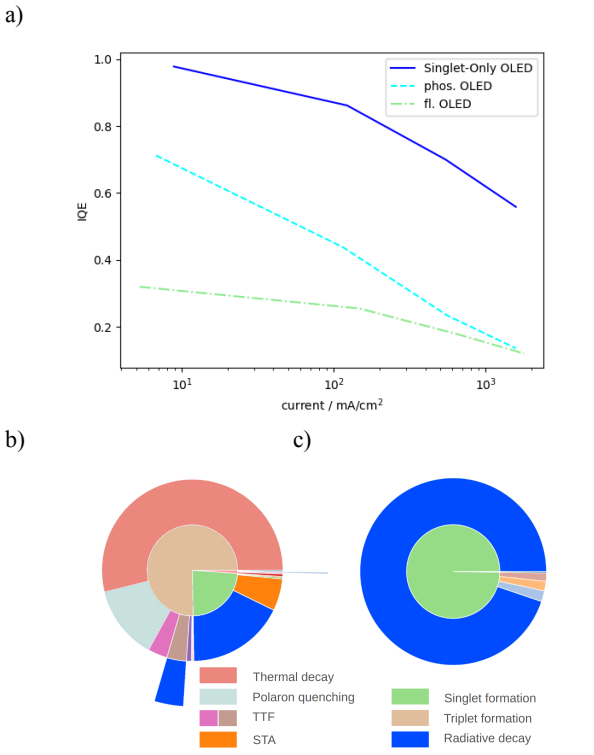


Figure 1. Demonstration of the Singlet-Only concept using parametric device simulations. a) IQE over current density for an EML with a typical phosphorescent emitter (dashed, cyan), a typical fluorescent emitter (dot-dashed, green) and a fluorescent emitter that fulfills the Singlet-Only criteria and is well aligned with the host-material (solid, blue). b) Exciton lifecycle of the fluorescent device with a standard emitter (left), exhibiting standard spin statistics with 25% singlets and 75% triplets (generation of excitons in the innermost circle). Triplets mostly undergo either thermal decay or polaron quenching. c) The Singlet-Only EML shows close to 100% singlet formation that mostly undergo radiative decay, resulting in close to 100% IQE at low currents in Fig. 1a).

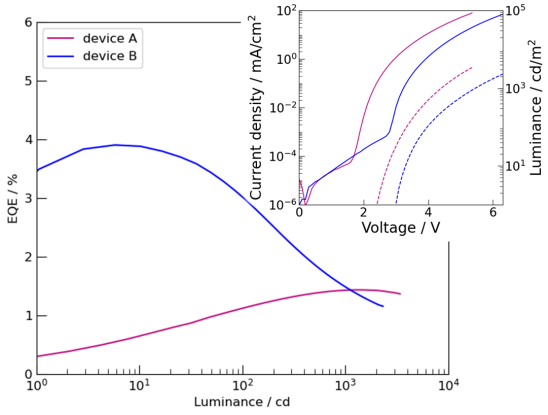
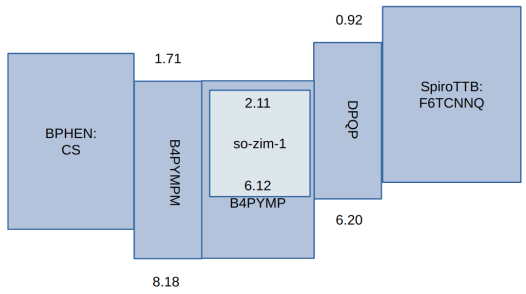


Figure 2. Experimental roll-of (EQE over luminance) and corresponding current density-voltage-luminance (J-V-L) characteristics of devices A and B. Data for device A is averaged over two pixels and for device B over four pixels.

(a)



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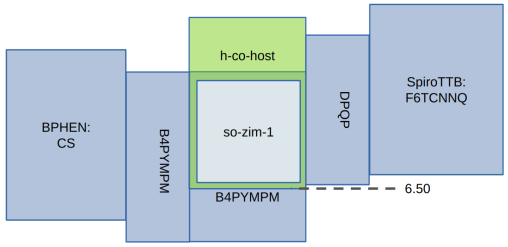
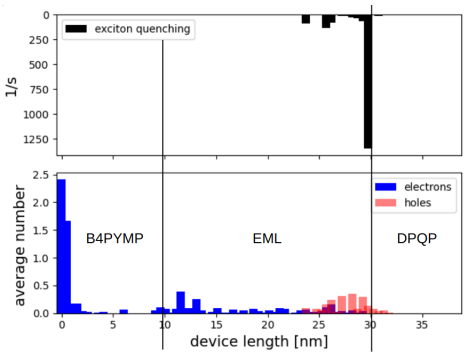


Figure 3. Energy cross sections of a) device A and b) an improved device with a co-host.

On the basis of insights from pre-screening via Nanomatch scientific software, two devices were generated: device A) BPHEN:CS/B4PYMP/B4PYMP:so-zim-1(4wt%)/DPQP/SpiroTTB:F6TCNNQ and device B) BPHEN:CS/BPhen/mSiTrz:so-zim-1(4wt%)/CzSi/CzSi:MoO3. EQE of both devices was measured as displayed in Fig. 2 with top EQE of 1.5 % and 4 %, respectively. These values correspond to typical fluorescent OLED performance without significant increase in efficiency as would be expected for a Singlet-Only emission system.

To understand performance bottlenecks in these devices, and to derive what prevents suppression of triplets, we conducted kMC simulations of device A, using rates computed with material properties derived from first principles. This multiscale simulation approach has been presented previously and was benchmarked against experimental data.(9,13,28) Simulations were limited to the subsystem of B4PYMP/B4PYMP:so-zim-1(4wt%)/DPQP with injection/transport layers simulated as effective electrodes with workfunctions of 1.4 and 5.6 eV respectively. The energy cross section of the device is depicted in Fig. 3a). HOMO and LUMO levels were computed with the multiscale workflow considering polarization effects within the film.(9) These simulations provided an internal quantum efficiency (IQE) of 7.8 %, which is in good agreement with the experimental EQE of 1.5 %, assuming a typical 20 % outcoupling efficiency.

(a)



(b)

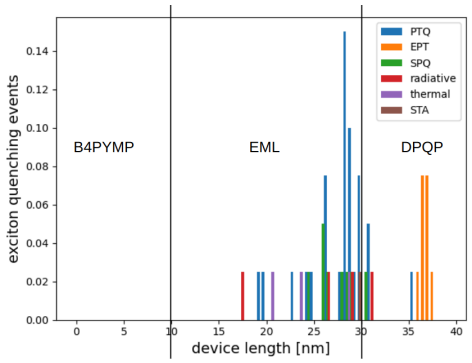


Figure 4. a) Charge carrier balance and total quenching profile over device cross section. Holes are trapped in the EML near the EML/DPQP interface. Quenching profile resolved by individual processes over device cross section. b) Large concentration of holes near the EML/DPQP interface leads to increased polaron quenching for both triplets (PTQ) and singlets (SPQ).

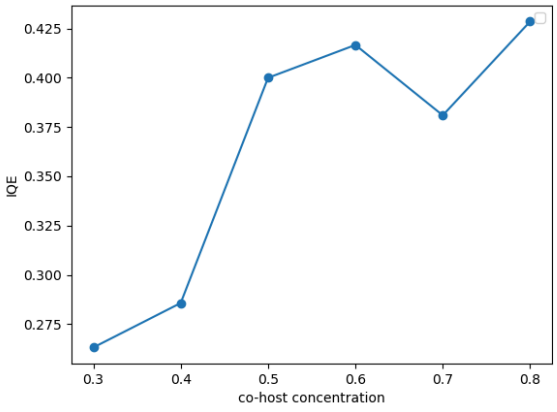


Figure 5. IQE of the Singlet-Only device using a co-host in dependence of the co-host concentration (mol) shows IQE > 40 % for co-host concentration around 50 %. This indicates a singlet-ratio significantly above 25 %.

Fig. 4 shows charge carrier balance and quenching processes over device cross section. We find an uneven charge carrier distribution with holes in the EML located near the DPQP interface. This charge carrier imbalance is induced by insufficient hole transport between emitter molecules with a large barrier to host molecules, whereas transport of electrons between emitters is supported by virtual states on host molecules (superexchange).(27) Ultimately, this trapping of holes near the DPQP layer leads to polaron quenching (PTQ, SPQ) as visible in Fig. 4b.

To improve hole transport, we introduce a co-host in the prototypical digital twin of device A, as illustrated in Fig. 3b. The barrier between HOMO levels of emitter and co-host was set to the barrier between LUMO levels of emitter and host, which was computed to be 0.4 eV. The resulting IQE for different co-host concentrations is displayed in Fig. 5. We find that for co-host concentrations above 50 %, IQE increases from 7.8 % (no co-host) to above 40 %. As only singlets can decay radiatively, this shows a significant deviation from standard spin-statistics with a singlet-ratio above 40 % in this system. We expect similar performance improvement for implementing a suitable co-host material in device B as well.

4. Conclusion

We propose a novel Singlet-Only emission system consisting of a fluorescent emitter with three specific properties, embedded into well aligned host materials, which prevents formation of triplets on the emitter. While an increased singlet-ratio cannot be derived from first experimental observation, simulations suggest that an increase of singlet ratio to above 40 % can be achieved by improved charge carrier balance. Next steps will include validation of these findings with experiment, and further improvement of the setup to tune singlet-ratio towards 100 %.

Using a tightly integrated approach of simulations and experiments allows rapid prototyping of emitter candidates with required properties and well-aligned host materials. We note that there is no interdependence between constraints for emitters and hosts, which increases chances of success to find suitable materials. Once successfully realized, the Singlet-Only OLED promises key advantages over existing technologies, such as IQE close to 100 %, complete absence of harmful triplets, while deploying materials that we expect to have a high level of chemical stability. The simple setup in the optimal case of a single emitter embedded in a single host promises large savings in both materials and production cost.

5. Acknowledgements

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6. References

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