Delocalizing Electron Distribution in Organic Molecules Towards High-Efficiency, Long-Lifetime Delayed Fluorescence

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Abstract

Here, we develop TADF emitters with delocalized electron distribution through a secondary acceptor, not only thermodynamically improving the intrinsic molecular stability in both excited and anionic states, but also dynamically fastening the reverse intersystem crossing process for a fast exciton consumption. The targeted compounds as emitters in OLEDs exhibited high maximum external quantum efficiencies of 27.9-37.1% and remarkably long LT95s (times decay to 95% of the initial luminance) of 380 and 648 h for blue and greenish devices at 1,000 cd/m^2.

Author Keywords

multi-resonance; electron distribution; high efficiency; high efficiency; high color purity

1. Introduction

Under electrical excitation, electrons and holes recombination would statistically generate a ratio of 25% singlet and 75% triplet excitons in organic light-emitting diodes (OLEDs). Over the past two decades, substantial efforts have been devoted into developing strategies to harness spin and exchange interactions that allows the control of singlet and triplet excitons to produce high device efficiencies.[1] The use of organic iridium complexes allows close to 100% efficient phosphorescence, and these are now widely used for red and green sub-pixels in current smart phone and television OLED displays. Although these approaches support the current successful commercial OLED display technology, new options for spin engineering to give emission efficiency are being actively investigated with the aim to find next-generation low-cost OLED materials. The Adachi group has pioneered the use of thermally activated delayed fluorescence (TADF) donor-acceptor emissive molecules, where the spatial separation of the photoexcited electron and hole lowers the exchange energy to thermally accessible levels.[2] This enables reverse intersystem crossing (RISC) from the non-emissive triplets to the emissive singlets. The slow RISC and radiative emission rates would extend exciton lifetimes from nanoseconds for standard Frenkel excitons out towards micro- or even milliseconds but, remarkably, high OLED efficiencies can also be achieved. However, the studies on improving molecular stability of TADF compounds are still lagged behind and the combination of a high efficiency and a good long-term stability is still a major conundrum of commercialization.

Though the complex underlying physics, triplet excitons involved bimolecular interactions, involving triplet-triplet annihilation (TTA), triplet-polaron annihilations (TPA) etc has been recognized as the main reason for the degradation of TADF compounds, whereby the generated energetically higher species will induce bond cleavage to produce radical fragments, which then participate in further radical addition reactions for even more degradation products. The solution to improve molecular stability should naturally include the accelerate in exciton consumption from the kinetic point of view and the strengthen of the bond dissociation energy (BDE) of molecules in excited and polaron states from the thermodynamic point of view, both favoring to reduce the chance for unwarranted chemical reactions. Till now, nearly all endeavors have been exclusively devoted into fastening RISC process to accelerate the triplet consumption by enlarging spin-orbital coupling (SOC) constant through mixing near energy degenerate charge transfer (CT) levels and localized triplet states and/or introducing heavy metal atoms. Consequently, RISC with a constant over 10^7 s^{-1} has been reported and afforded blueish green device with a LT90 (time required to decay to 90% of the initial luminance) of over 35 h at an initial luminance of 5,000 cd/m^2.[3] Further accelerating exciton consumption can also be done by using TADF compounds as sensitizers for a fluorescent final emitter, termed as TADF-sensitized fluorescence (TSF) or hyperfluorescence.[4] In this way, a "one-way" rapid Förster energy transfer from TADF sensitizer to final emitter can reduce the number of spin-flip transition cycles between singlet and triplet in the TADF molecules and thereafter quickening the exciton consumption for a significant prolonged device lifetime. Particularly, using multi-resonance compounds as the final emitters in TSF not only improving device efficiency and stability, but also narrowing the emission spectra for high color-purity.

These early reports on blue TADF device lifetime were encouraging, but the subsequent development has been slow and there is still long way to go for commercialization in real products. One more fundamental and essential issue remains for this goal, that is though great efforts in kinetic dynamics, works aiming to improve the intrinsic stability of TADF molecules from a thermodynamics perspective are kind of rare, let alone the strategies that can integrate both impacts. Here, we proposed a general molecular design that can take account of both chemical bond stabilization and fast exciton consumption, achieving a high efficiency and a reliable lifetime.[5] This molecular design is accomplished by strategically delocalizing the electron distributions in TADF molecules through a secondary acceptor, which not only thermodynamically stabilizes the molecule intrinsic stability in both excited and negative polaron states, but also dynamically fastens the RISC process for a fast triplet consumption. Both favor a good long-term stability under electrical excitation, thus affording exceptionally long device lifetimes and high efficiency when used as both emitters and sensitizers.

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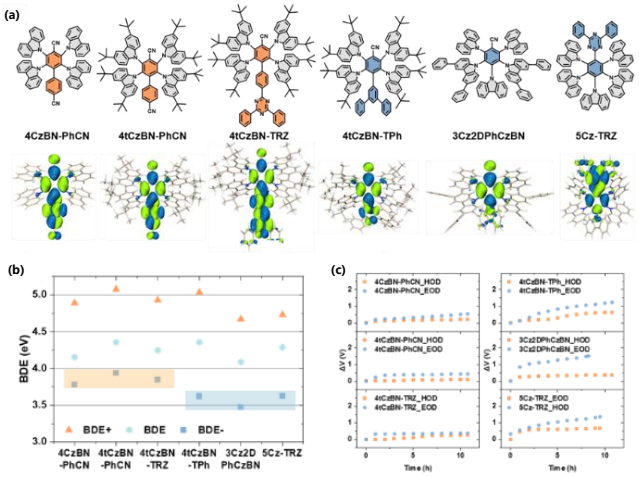

Figure 1. (a) Molecular structures and LUMO distributions of electron-delocalizing TADF molecules and contrast molecules; (b) BDE values of the molecules; (c) Film photoaging diagram of the molecules; (d) Voltage rise plots in electrical aging of single-carrier devices.

2. Experimental Results and Discussion

2.1 Material Design: To demonstrated this inspiration, a second acceptor group as introduced to the para-position of CN units, forming 4CzBN-PhCN, 4tCzBN-PhCN and 4tCzBN-TRZ, respectively. PhCN and TRZ were chosen as the second acceptor owing to the proved stability of such groups as illustrated in Figure 1. For a better comparison, 4tCzBN-tPh with a tert-butyl phenyl (tPh) group as also developed, of which the same strategy was adopted in a recently reported stable blue TADF molecular. Besides, we also studied the stable 5Cz-TRZ and 3Cz2DPhCzBN for companions, both of which have been reported to provide long lifetimes in devices in the greenish region.

Firstly, we studied the HOMO and LUMO distributions of those compounds by Gaussian 09 using B3LYP/6-31G (d,p) as the basis. The LUMO distributions of those compounds varied with each other as illustrated in **Figure 1a**. The LUMO distributions of **t**he targeted molecules are extended to the secondary acceptor segments, being more delocalized compared with other reference compounds. It should be mentioned that though LUMO also extended to the attached phenyl on tPh unit, the electron delocalization degree should be relatively smaller compared with the targeted molecules. The BDE of all C-N bonds in those compounds were then calculated as depicted in **Figure 1b**. Similar to other TADF emitters, all those compounds still showed the lowest energy BDE-. Interestingly, compared with the reference compounds, all compounds with a secondary acceptor showed significantly higher BDE- values of 3.78, 3.94 and 3.84 eV for 4CzBN-PhCN, 4tCzBN-PhCN and 4tCzBN-TRZ, respectively, suggesting that the potentially increased molecular stability. The enhanced BDE(-) of the targeted molecules can be assigned to the increased electron affinity of the molecular. According to the Hess's law, BDE(-)=BDE(n)+EAm-EAx, where EAm and EAx stand for the electron affinity (EA) of the radical anion after dissociation and the intact molecule. Introducing a secondary acceptor groups would naturally enlarge EAm and thus favors a large BDE(-). Essentially, two typical ways to increase EAm are introducing strong electron withdrawing groups and extending conjugation length. In 4tCzBN-tPH, though the delocalized structures, the lack of electron withdrawing groups limited the increase in BDE(-).

The stability of those molecules in positive and negative states can be experimentally demonstrated by hole- and electron -only devices (HODs/EODs) with device structures of ITO/ HAT (5 nm)/ NPB (30 nm)/ EML (30 nm)/ HAT (5 nm)/ Al and ITO/ Cs2CO3 (1 nm)/ DPPyA (30 nm)/ EML (30 nm)/ DPPyA (30 nm)/ LiF (0.5 nm)/ Al, respectively. The carrier-only devices were aged under the operating conditions of current stress with a constant current density of 20 mA/cm^2 and the voltage changes were recorded. Previous works have pointed out that under electrical stress, the molecular degradation products will act as the fixed charge sites to repulse the vicinal charge and thus yield a voltage rise. According to **Figure 1d,** the voltages of EODs of all the samples rose faster than their HODs, indicating a relatively better stability of the molecules in cationic states than the anionic states. More importantly, the EODs of 4CzBN-PhCN, 4tCzBN-PhCN and 4tCzBN-TRZ have only inconspicuous voltage rise, but the voltage rise of the EODs of 4tCzBN-TPh, 3Cz2DPhCzBN and 5Cz-TRZ are much more evident. It comes to a conclusion that the three molecules with electron-delocalization have a better chemical stability in both cationic and anionic states while their three counterparts may more possibly undergo bond dissociation process by the acceptance of negative charges.

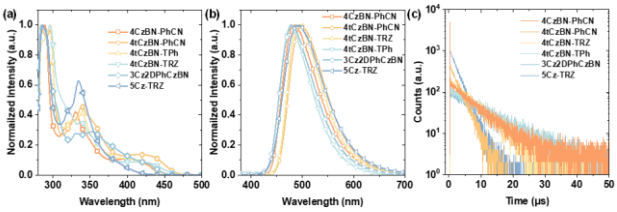

Figure 2. (a) UV-Vis absorption spectra, (b) photoluminescence spectra of the TADF materials; (c) transient photoluminescence decay curves of the TADF materials in dilute oxygen-free toluene.

2.2 Material Design: The photophysical properties of those compounds were further studied in dilute toluene (10^{-5} M) as illustrated in Figure 2, Figure S and Table 1, aiming to confirm the effect of this electron delocalizing strategy from a kinetic viewpoint. **Figure 2a** depicts the UV-Vis absorption spectra of those compounds, all showing similar absorption peaks around 290 nm and 340 nm that arise from the n-p* or p-p* transition of carbazole moieties. Broad band with wavelength above 400 nm were also recorded due to the CT transitions, among which 4tCzBN-PhCN gains the strongest absorption intensity, indicating the largest oscillator strength (*f*) of the S_0-S_1 transition. The emission spectra of those compounds were provided in **Figure 2b** and the colors of all those compounds are in the range of 478 nm-497 nm, corresponding to sky-blue to greenish region. Starting from 4tCzBN-TPh, which possesses an emission peak of 478 nm, 4tCzBN-PhCN and 4tCzBN-TRZ showed slightly red-shifted emission maximums of 497 and 492 nm due to additional electron-withdrawing groups. Interestingly, 4CzBN-PhCN, as a t-butyl-free analog of 4tCzBN-PhCN, exhibited a 11 nm blue-shift owing to the reduced electron-donating ability of the donors. From the onset of those fluorescence spectra, similar S_1 energies in the range of 2.72 eV-2.84 eV were thereafter being obtained, facilitating the comparison of the molecule stabilities. The phosphorescent spectra of those compounds were also taken under 77 k with a 10 ms delay as illustrated in Figure S, obtaining triplet energies of 2.63-2.81 eV.

Consequently, small ΔE_{STS}<0.05 eV were obtained for those compounds except for 3Cz2DPhCzBN (0.15 eV), of which the triplet energy is relatively lower due to the phenyl substituted carbazole acceptors.

The photo-luminance quantum yields (PLQYs) of those compounds in toluene were also measured, being 0.160, 0.133, 0.140, 0.131, 0.150 and 0.060 before degassing and 0.999, 0.997, 0.973, 0.989, 0.90 and 0.99 for 4CzBN-PhCN, 4tCzBN-PhCN, 4tCzBN-TRZ, 4tCzBN-TPh, 3Cz2DPhCzBN and 5Cz-TRZ, respectively, after bubbling nitrogen. The PL decay curves of those emitters recorded at an excitation wavelength of 360 nm and clear bi-exponential decay characteristics were observed, suggesting the TADF properties for all compounds.

Compared with the reference 4tCzBN-TPh, 3Cz2DPhCzBN, whose delayed lifetime is over 9.5 μs, the targeted compounds exhibited obvious shorter τ_{DS}< 6.5 μs, particularly for 4tCzBN-PhCN (2.4 μs). To the best of our knowledge, a quick exciton consumption dynamically favors to suppress exciton annihilations. Therefore, besides thermodynamically stabilizing the molecule in both excited and negative polaron states, this electron delocalizing strategy also dynamically favors to enhance molecular stability. Table 1 also provided the rate constants of those emitters. It is worth noting that the targeted molecules showed both high rate constants of radiative decay and RISC, with the former over 10^7 s^{-1} and the latter over 10^6 s^{-1}. Particularly, 4tCzBN-PhCN showed a highest k_r of 2.47×10^7 s^{-1} and an excellent k_{RISC} of 31.2×10^6 s^{-1}. The reference compounds, however, showed a trade-off between k_r and k_{RISC}. The reason for the quick exciton dynamic processes should be attributed to, on one hand, the more delocalized LUMO distributions, as it increases the transition dipole moment to balance a large oscillator strength and a small ΔE_{ST}. On the other hand, the multiple donors structures also favors to induce a dense manifold of triplet states with CT/LE hybrid character are formed which are confirmed by excitation analysis, thus facilitating a large spin-orbital coupling for efficient spin flip transitions. The coefficiencies of SOC (λ_{SOC}) between T_2 and S_1 were calculated to be 0.71, 0.66 and 0.60 cm^{-1} for 4tCzBN-PhCN, 4tCzBN-TRZ and 4tCzBN-TPh, respectively. Those large λ_{SOC}s well explained the efficient RISC process of those compounds. It should also be noted that, 5Cz-TRZ also showed a rapid exciton consumption with a delayed lifetime of 2.2 μs and a cutting-edge kRISC of 7.6×107 s-1. However, this compound showed a relatively poor stability under UV irradiation and eletrical excitation in EODs. This further evidenced that besides a rapid dynamic process, an intrisinc stable molecular structure is also enssential.

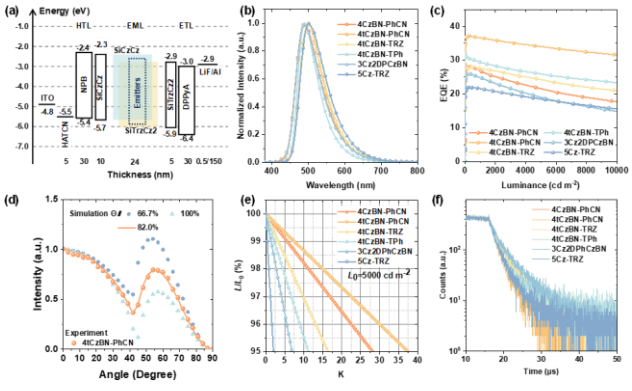

Figure 3 (a) Diagram of the TADF-device structure. (b) Electroluminance spectra of the TADF-devices at 1000 cd/m^2. (c) EQE-Luminance relationship of the TADF-devices. (d) Angle-dependent PL spectra of 4tCzBN-PhCN-doped in SiCzCz: SiTrzCz2 films. (e) Operational lifetimes of the TADF-devices. (f) Transient electroluminance decay curves of the TADF-devices

The performances of those emitters in OLEDs were then evaluated with the following architectures: ITO/ HATCN (5 nm)/ NPB (30 nm)/ SiCzCz (10 nm)/ SiCzCz: SiTrzCz2: TADF emitter (24 nm, 0.60:0.40:0.30 w/w/w)/ SiTrzCz2 (5 nm)/ DPPyA: Liq (30 nm, 1:1) / LiF (0.5 nm)/ Al (150 nm), where 1,4,5,8,9,11-hexaazatriphenylene hexacarbonitrile (HATCN) and LiF were used as hole- and electron- injection layer; 4,4-N,N-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (NPB) and 9,10-bis(6-phenylpyridin-3-yl)anthracene (DPPyA) doped with 8-Hydroxyquinolinolato-lithium (Liq) served as hole- and electron-transporting layer, respectively. Notably, to avoid the influence of host materials, a proved stable exciplex-forming system, SiCzCz: SiTrzCz2, was chosen as the host, where SiCzCz represented while SiTrzCz2 is, respectively. The energy level diagram and the characteristics of the fabricated OLEDs are shown in **Figure 3**. Pristine SiCzCz and SiTrzCz2 films were inserted between transporting layers and EMLs, facilitating charge recombination on the host to guarantee wide recombination zone for better device stability.

Figure 3b provided the EL spectra of those devices taken at a luminance of 1,000 cd/m2. Similar to the PL results, emission maximums in the range of 478 nm-501 nm were obtained, corresponding to sky-blue to greenish colors. The similar emission colors render it possible to compare the molecular stabilities. The EQE-luminance characteristics were depicted in Figure 3c and all devices showed high maximum EQE values over 20%. Particularly, the device based on 4tCzBN-PhCN not only presented the highest EQE_{max} of 37.1% , but also exhibited extremely small efficiency roll-off with EQE remaining 36.4% and 34.2% at high luminance of 1,000 cd/m2 and 5,000 cd m^{-2}, respectively. The nearly negligible efficiency roll-off can be attributed to the fast exciton consumption of this emitter, which benefits to suppress exciton annihilations under high luminance. The other two targeted molecular showed EQE_{max}s of 28.0% and 27.9%, which remained 26.6% and 27.6% at 1,000 d/m^2, respectively. Interestingly, the efficiency roll-off behaviors of those compounds are nearly in agreement with their τ_{DS} and the shorter ones would lead to a smaller efficiency roll-off. To confirm the origin of those cutting-edge efficiency, we further characterized the angle-dependent PL intensities of the p-polarized light emitted from the 30nm-thick tertiary doped EML to study the orientations of the emitting dipole orientation (EDO) of those emitters. As illustrated in **Figure 3d**, relatively high ratios of the horizontal EDO ($\Theta_{//}$) in the range of 75%-82% were obtained. Previous works have validated the a high $\Theta_{//}$ would greatly enhance outcoupling efficiency of devices, partly accounting for a high EQE.

Next, we assessed the continuous operation stability of those devices under a constant current density at an initial luminance of 5000 cd/m2. A marked enhancement of operation stability in the molecules with secondary acceptors were observed compared with reference emitters. The LT95s (the time required to decay to 95% of the initial luminance) were 28.2 h, 37.6 h and 16.4 h for 4CzBN-PhCN, 4tCzBN-PhCN and 4tCzBN-TRZ based devices, while being only 11.2 h, 6.9 h and 2.0 h for 4tCzBN-TPh, 3Cz2DPhCzBN and 5Cz-TRZ, respectively. Using a regular degradation acceleration factor (n) of 1.7, the LT95s for devices with 4CzBN-PhCN, 4tCzBN-PhCN and 4tCzBN-TRZ at an initial luminance of 1000 cd/m2 can be extrapolated to be 434 h, 579 h and 253 h,

respectively, using an equation of LT95 (1000 cd/m2)=LT95 (5000 cd/m2) × (5000 cd/m2/1000 cd/m2)^n. Such significant lifetime enhancements here should be a combination of the thermodynamically stabilized molecule structures and the dynamically fastened exciton consumptions. The EL decay curves of those devices were taken at luminance of 1000 cd/m2 as shown in Figure. Compared with their PL lifetimes, a similar trend was observed for the EL results with the fastest ones being 4tCzBN-PhCN and 5Cz-TRZ while the slowest ones being 3Cz2DPhCzBN. It is reasonable that 4tCzBN-PhCN based device showed the longest LT97 owing to the both stable molecular structure and quick exciton consumption of the emitter. The 4CzBN-PhCN, though its moderate exciton consumption rate, also showed a second best LT97 owing to its stable molecular structure. As comparison, 5Cz-TRZ, though possessing a fast exciton consumption, only provided the shortest LT97 owing to its poor molecular intrinsic stability. Those results clearly unveiled the crucial importance of thermodynamically stabilizing molecule structures. It should be further pointed out that with a different device, the LT95% of nearly 200 h can be obtained for 3Cz2DPhCzBN and 5Cz-TRZ based device, which is longer than the results in our structure, but still shorter than the lifetimes obtained in our targeted molecules. This suggest that by further optimizing the functional materials, even longer lifetime can be further obtained.

3. Impact and Outlook

In this article, we found that the introduction of a second acceptor in TADF molecules can finely delocalize the electron distribution, facilitating not only a thermally stabilized molecular structure in both excited and negative states, but also a fast exciton consumption process. The targeted molecules showed a shortest delayed lifetime of only 2.2 us and negligible decay under UV irradiation. A highest EQEmax in the range of 27.9-37.1% was obtained. Furthermore, those devices showed alleviated efficiency roll-off with a highest EQE of 34% at 5000 cd/m2 (92% of the EQEmax). More importantly, remarkably long LT95s of 380 and 648 h for blue and greenish devices were observed at 1,000 cd/m^2, which is five to over tenfold higher than the reference device based on previously reported stable TADF emitters with similar colors. Our work here validated the great potential of TADF compounds as emitters or sensitizers in OLEDs, representing an important step towards improving the stability of TADF molecules, paving the way to efficient and stable TADF and hyperfluorescent OLEDs.

4. Acknowledgments

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5. References

1. Tang C W et al. Organic electroluminescent diodes. Applied Physics Letters 1987, 51: 913-915.
2. Uoyama H et al. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 2012, 492: 234–238.
3. Cui L S et al. Fast spin-flip enables efficient and stable organic electroluminescence from charge-transfer states. Nat. Photonics 2020, 14: 636–642.
4. Zhang D et al. High-Efficiency Fluorescent Organic Light-Emitting Devices Using Sensitizing Hosts with a Small Singlet–Triplet Exchange Energy. Advanced Materials 2014, 26, 5050-5055.
5. Huang T et al. Delocalizing electron distribution in thermally activated delayed fluorophors for high-efficiency and long-lifetime blue electroluminescence. Nature Materials 2024, 23:1523–1530.