Konformacinės netvarkos sąlygoti emisijos reiškiniai kietuosiuose TADF junginių sluoksniuose

Conformational disorder enabled emission phenomena in TADF compound films

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Thermally activated delayed fluorescence compounds offers an elegant way to retrieve triplet excited states without involving any expensive heavy atoms, following simple chemical synthesis and providing sufficient chemical stability [1]. OLED devices with TADF emitters provides excellent external quantum efficiency, exceeding 30%, pronounced lifetime and wide selection of emission color [2,3]. Recovery of triplet states in TADF compounds is enabled by minimizing singlet-triplet energy gap (ΔE_{ST}) towards the values comparable to thermal energy at room temperature. The most common design approach for lowering ΔEST is based on the separation of molecular frontier orbitals in HOMO and LUMO. This is usually achieved by constructing TADF compounds from electron-donating (D) and electron-accepting (A) units, loosely bound with nearly perpendicular orientation. Specific molecular structure of TADF compounds, when D and A units are loosely bound, makes its emission properties dependent on the D-A twisting angle. In rigid solid-surrounding, TADF compounds froms conformers with different D-A twisting angles, theredire different S_1 energies and ΔE_{ST} values. Such conformational disorder results in the undesirable effects, such as prolongation of TADF lifetime or emission energy instability [4,5].

Moreower, TADF compounds doped in solid hosts are prone to undergo solvation effects, similar to those as in solution state. Emission peak shifts and changes in emission decay rates usually follows the solid-state solvation (SSS). However, here we show that typical SSS behavior in heavily doped TADF films of **5tCzMeB** (see Fig. 1) could be of completely different origin, mistakenly attributed to SSS.

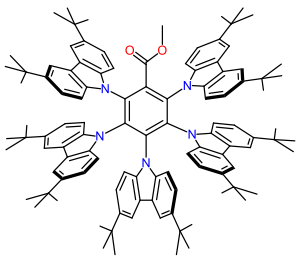

Fig. Molecular structure of **5tCzMeB**.

Typically, increasing doping load was found to redshift the emission peak wavelength and enhance rISC rate. However, the more in-depth analysis revealed that SSS actually is negligible and both phenomena are caused by the specific behavior of delayed emission. Increasing concentration of TADF compound was shown to enhance the concentration quenching of long-lived delayed fluorescence from conformer states with the largest singlet energy, eventually leading to gradual redshift of delayed emission peak wavelength (see Fig. 2). Concomitantly, the loss of long-lived delayed fluorescence entailed reverse intersystem crossing rate enhancement, though the rate-governing ^{3}CT-^{3}LE energy gap was gradually increasing. The observed phenomena are highly unwanted, burdening molecular structure and OLED performance optimization.

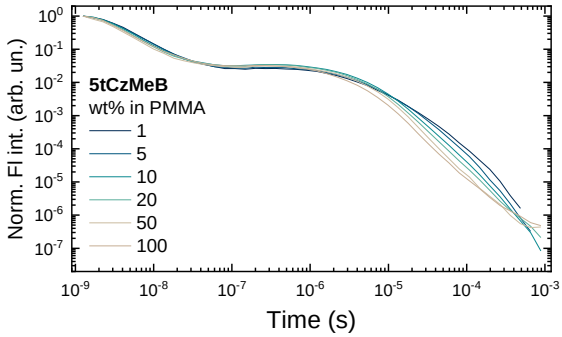

Fig. 2 Fluorescence decay transient of TADF compound **5tCzMeB** at different doping load in PMMA.

Keywords: TADF, disorder, triplet, diffusion, exciton.

References

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