Blocking Energy-Loss Pathways for Efficient All-Fluorescent Solution-processed Organic Light-emitting Diodes by Introducing Polymer Additive

Ming Zhang\(^{1,2}\), Cai-Jun Zheng\(^*\), Kai Wang\(^2\), Hui Lin\(^1\), Si-Lu Tao\(^*\), and Xiao-Hong Zhang\(^*\), \(^1\)
1 School of Optoelectronic Information, University of Electronic Science and Technology of China (UESTC), Chengdu 610054, PR China.
2 Functional Nano and Soft Materials Laboratory (FUNSOM) and Collaborative Innovation Center of Suzhou Nano Science and Technology Soochow University, Suzhou, Jiangsu 215123, PR. China.
E-mail addresses: zhengcaijun@uestc.edu.cn (C. J. Zheng), silutao@uestc.edu.cn (S. L. Tao), xhzhang@mail.ipc.ac.cn (X. H. Zhang).

Abstract: Organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence-sensitized conventional fluorescence dyes (TSCF) offer the possibility of realizing an ultimate high efficiency and long-term stability devices through solution process. However, the currently reported TSCF-OLEDs easily suffer the harmful Dexter energy transfer (DET) process and aggregation induced quenching (ACQ) effect. Herein, we proposed a new strategy to suppress the DET and ACQ effect by introducing a polymer material into TSCF system, achieving high efficiency and stability of TSCF-OLEDs. The introducing polymer material into TSCF system can not only increase the intermolecular distance between TADF matrix and traditional dyes, further restraining the harmful DET process and ACQ effect, but also improve the solubility and film quality of all TSCF system. Based on this fact, the 2-(2,7-di(9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)dibenzo[b,d]thiophene 5,5-dioxide (2Cz-DMAC-BTB) sensitizing 2,8-Di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb) solution-processed device Y\(_2\) with poly ethlene oxide (PEO) was firstly fabricated and exhibits a higher maximum EQE of 6.6 % and longer half time (LT\(_{50}\)) of 64 hours comparing to that of Y\(_1\) without PEO. Subsequently, the TSCF-solution-processed device R\(_2\) with PEO shows a maximum EQE\(_{\text{max}}\) of 13.1 % and LT\(_{50}\) of 107 hours. These results adequately demonstrate the validity of our proposed strategy and provide a new route for developing more efficient all-fluorescent solution-processed TSCF-OLEDs.

1. Introduction
Organic light-emitting diodes (OLEDs) have aroused extensive attention in the academia and industry since they possess great potential applications in flat-panel displays, solid-state lighting, and wearable electronics applications.[1-4] It is well known that the recombination of holes and electrons under electrical excitation typically generates 25 % singlet excitons (S\(_1\)) and 75 % triplet excitons (T\(_1\)).[5, 6] Comparing to the conventional fluorescent dyes possessing only 25 % S\(_1\) and phosphorescent emitters containing heavy metals into the organic aromatic frameworks to reach 100 % internal quantum efficiency, theoretically, metal-free thermally activated delayed fluorescent (TADF) emitters could
harvest both $S_1$ and $T_1$ for theoretically 100% IQE via effective reverse intersystem crossing (RISC) process.[7-10] Till now, large amount of TADF emitters based-OLEDs by vacuum evaporated method have achieved remarkably high efficiencies over 30% external quantum efficiency (EQE), which are ahead of the best phosphorescent OLEDs.[2, 7] As an alternative choose, solution processes involving spin-coating or ink-jet printing have emerged as preferred methods due to easy fabrication procedures, low-cost device fabrications and large-area applications.[6, 7, 11-13] Actually, the performances of several solution-processed devices have reported to be comparable to their corresponding devices via vacuum deposition.[14-18] Therefore, developing solution-processable TADF emitters or TADF as sensitizing hosts for solution-processed OLEDs is highly desired.

For an ideal TADF emitter, the twisted intramolecular charge transfer (TICT) framework is commonly adopted, endowing the emitters with moderate singlet excitons radiative rates ($k_r$) and small singlet-triplet energy gap ($\Delta E_{ST}$).[3, 7, 13, 19] However, the dilemma for a TADF emitter keeps a very delicate balance that it is required to simultaneously achieve a high radiative decay rates and small $\Delta E_{ST}$. The tradeoff can be broken by delivering the singlet energy of TADF emitters to traditional dyes via the efficient Förster resonance energy transfer (FET) process.[9, 12] Meanwhile, considering the narrow full-width at half maximum (FWHM) and excellent stability of traditional dyes, the colour purity and device stability of all-fluorescent solution-processed OLEDs can be efficiency improved. Thus, TADF sensitizing conventional fluorescent dyes (TSCF) devices via solution process have been widely investigated.[9] As illustrated in Figure 1a, the TSCF solution-processed devices always occur efficient FET process along with Dexter energy transfer (DET). However, these reported TSCF-devices easily suffer the serious DET process further resulting in serious triplet-triplet annihilations (TTA) and aggregation induced quenching (ACQ) effect. Obviously, a feasible and promising approach to develop TSCF-based solution-processed OLEDs is extremely urgent and important.

![Figure 1](image)

To solve this issue, we proposed a novel strategy to suppress the DET and ACQ effect by introducing a polymer material into TSCF system, achieving high performance of all-fluorescent solution-processed OLEDs. In such a method, on one hand, the introducing polymer material into TSCF system can increase the intermolecular distance between TADF host and traditional dyes, further restraining the harmful DET process and ACQ effect while not affecting their FET process. On the other hand, polymer molecule have good solubility and film forming properties, and the solubility and film quality of all TSCF system would be remarkably improved. Based on this fact, the reported 2-(2,7-di(9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)dibenzo[b,d]thiophene 5,5-dioxide (2Cz-DMAC-BTB) and poly ethene oxide (PEO) were chosen as TADF host and assistant dopant, respectively. Yellow fluorescent 2,8-Di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetraacene (TBRb) and red fluorescent tetraphenyl dibenzoperiflanthene (DBP) were used as emitters. The 2Cz-DMAC-BTB sensitizing TBRb solution-processed devices Y1 without PEO and Y2 with PEO display the similar EL spectra, turn-on voltage and maximum EQEmax of 3.7 % and 6.6 %, respectively. Meanwhile, the half lifetime (LT50) of
Y1 and Y2 is 13.6 and 64 hours, respectively. To adequately demonstrate the feasibility of this strategy, the DBP-based solution-processed devices R1 without PEO and R2 with PEO were finally fabricated. As expected, the R2 exhibits a higher maximum EQE$\text{max}$ of 13.1 % and longer LT$\text{50}$ of 107 hours comparing to that of R1. These results adequately demonstrate the validity of our proposed strategy and also unfold a new route to develop more efficient all-fluorescent solution-processed TSCF-OLEDs.

2. Experimental Section
Device fabrication and measurement: 110 nm-thick indium tin oxide (ITO) glasses substrates with a sheet resistance of 30 Ω per square were firstly cleaned with cleaning agent, deionized water, acetone, ethanol. Then dried in the oven at 120°C for 2 h and treated with UV-ozone for 30 minutes. Subsequently, the PEDOT:PSS 8000 (CLEVIOS™ P VP CH 8000) was filtered by using filtered (0.45 μm Poly tetra fluoroethylene membrane) and spin-coated to prepare the 40 nm hole-injection layer onto the ITO glass substrate via using 4000 rpm/min under ambient atmosphere. And then the ITO substrate containing PEDOT:PSS was annealed at 120 °C for 30 min to remove residual water and transferred into the nitrogen atmosphere glove-box containing less than 1 ppm oxygen and moisture. Later, the filtered 10 mg mL$^{-1}$ chlorobenzene solution was further spin-coated onto the PEDOT:PSS layer to finish the EMLs preparation and placed in the nitrogen atmosphere glove-box for 20 min to remove residual solvent. For all solution-processed devices, 5 nm TmPyPb was subsequently thermally evaporated onto the ITO substrates as hole-blocking layer at rate of 1 Å s$^{-1}$. And the electron-transporting layer TPBi was then thermally evaporated to make a 40 nm onto the ITO glasses at a rate of 1 Å s$^{-1}$. Finally, the 1 nm-thick of LiF and a subsequently 100 nm-thick of aluminium were thermally evaporated in high vacuum (10$^{-6}$ mbar) at the rates of 0.1 and 10 Å s$^{-1}$, respectively. All solution-processed devices were prepared and placed in the evaporation instrument for 30 min. The current-voltages characteristics of all devices were tested by a computer-controlled Keithley 2400 SourceMeter under ambient atmosphere. Meanwhile, their EL spectra, CIE coordinates and FWHM were obtained through a Spectrascan PR650 photometer. CEs, PEs and EQEs of all devices were calculated from the current density, luminance, and EL spectrum, assuming a Lambertian distribution. The device lifetime was measured through a 64-channel ZJLS-4 type OLED life aging testing system in the constant current mode at room temperature.

3. Result and discussion
In our previous work, the green TADF emitter 2Cz-DMAC-BTB was reported to attain a high EQE of 14.0 % in the solution-processed non-doped device.[16] Due to high radiative decay rates ($k_r$) and small $\Delta E_{ST}$, it can act as the excellent TADF host for solution-processed OLEDs, realizing even better performance than those of conventional host materials, such as 4,4',4''-Tri-9-carbazolyltriphenylamine (TCTA) et al. The classical long-chain polymer materials poly ethylene oxide (PEO) is chosen as the polymer additive.[20] Meanwhile, the yellow fluorescent 2,8-Di-tert-butyl-5,11-bist(4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb) and red fluorescent tetraphenyldibenzopiperiflanthe (DBP) are chosen as emitters to fabricate all-fluorescent solution-processed TSF-OLEDs.[21] Meanwhile, the HOMO energy levels of dopants are lower than that of 2Cz-DMAC-BTB, which can not only helpful to form the “barrier-free” device structure, but also effectively minimize the trapping effects on dopants.[22] Figure 2b shows the chemical structures of these materials used in this work and the proposed energy level diagram of devices.
According to our proposed strategy, the electroluminescence (EL) performance of TSCF-OLEDs were subsequently evaluated. We firstly fabricated the all-fluorescent TSCF-OLEDs by employing the 2Cz-DMAC-BTB-sensitized TBRb with PEO and without PEO as emitting material layers, respectively. As illustrated in Figure 2a, the solution-processed devices structure are as follows: Indium tin oxide (ITO)/PEDOT:PSS (40 nm)/EMLs (60 nm)/TmPyPb (5 nm) /TPBi (40 nm)/LiF (1 nm)/Al, where the emitting material layers (EMLs) respectively were 2Cz-DMAC-BTB: (6wt %)TBRb for Y1 and 2Cz-DMAC-BTB:(2 wt %)PEO:(6wt %) TBRb for Y2. Indium tin oxide (ITO) and LiF/Al were regarded as the anode and cathode, respectively. (1,3,5- tri(m-pyrid-3-yl-phenyl)benzene) TmPyPb and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) were respectively used as the hole-blocking layer and electron-transporting layer. As shown in Figure 3, the TSCF-OLEDs Y1 without PEO and Y2 with PEO display the same EL spectra and turn-on voltage, respectively, which indicates the addition PEO with good carrier transporting properties and no change its luminescent properties. Meanwhile, the devices Y1 and Y2 exhibit maximum current efficiency (CE) of 10.2 and 15.3 cd A\(^{-1}\), power efficiency (PE) of 3.5 and 9.4 lm W\(^{-1}\), and external quantum efficiency (EQE) of 3.7 % and 6.6 %, respectively. Besides, we further assessed the EL stability of Y1 and Y2. As shown in Figure 4a, the half lifetime (LT\(_{50}\)) of Y1 and Y2 is 13.6 and 64 hours at initial luminance of 100 cd m\(^{-2}\), respectively. Obviously, with the assistance of PEO, the EL efficiency and stability of all-fluorescent solution-processed OLEDs based on TBRb emitter is effectively improved, which directly prove the feasible of our proposed strategy.
Figure 3. a) Voltage-Luminance-Voltage-Current density, b) EQE-Luminance, c) EL spectra for the TBRb doped in 2Cz-DMAC-BTB solution-processed devices; d) Voltage-Luminance-Current density; e) EQE-Luminance; f) EL spectra for DBP doped 2Cz-DMAC-BTB solution-processed devices.

Table 1 The summary of these solution-processed devices performance.

| Devices | Von a) [V] | λ b) [nm] | Luminance c) [cd m\(^{-2}\)] | Max. CE/PE/EQE d) (cd m\(^{-2}\)/lm W\(^{-1}\)/%) | At 500cd m\(^{-2}\) e) Voltage | EQE f) | CIE g) (x, y) | Lifetime h) (hours) |
|---------|------------|----------|-----------------------------|---------------------------------|-------------------------|--------|----------------|-------------------|
| Y1      | 4.3        | 576      | 1001                        | 10.2/6.5/3.7                    | 7.9                     | 2.4    | (0.53, 0.46)   | 13.6              |
| Y2      | 4.2        | 576      | 1506                        | 15.3/9.4/6.6                    | 6.6                     | 4.9    | (0.53, 0.46)   | 64                |
| R1      | 3.2        | 608      | 1557                        | 11.4/10.2/6.9                   | 6.2                     | 4.5    | (0.58, 0.39)   | 61                |
| R2      | 3.3        | 612      | 2756                        | 21.9/16.7/13.1                  | 5.3                     | 5.9    | (0.58, 0.39)   | 107               |

a) Turn-on voltage at 1 cd m\(^{-2}\);
b) The emission peak at 1000 cd m\(^{-2}\);
c) The maximum luminance;
d) Max. CE/PE/EQE: maximum current efficiency/ power efficiency/ external quantum efficiency;
e) The corresponding voltage and efficiency at 500 cd m\(^{-2}\);
f) The CIE values recorded at 1000 cd m\(^{-2}\);
g) Device lifetime measured at an initial luminance of 100 cd m\(^{-2}\).

To further confirm the universality of this strategy for all-fluorescent solution-processed OLED, another classical red emission tetraphenyldibenzopeliflantanthe (DBP) was chosen as dopant to fabricate the solution-processed OLEDs. Then, the same configuration of ITO/PEDOT:PSS (40 nm)/EMLs (60 nm)/TmPyPB (5 nm)/TPBi (40 nm)/LiF (1 nm)/Al was used to prepare the solution-processed TSCF-OLEDs. Both 2Cz-DMAC-BTB: (1.5 wt %)DBP and 2Cz-DMCC-BTB: (2 wt %) PEO: (1.5 wt %) DBP were served as the EMLs, respectively. As expected, the R1 without PEO and R2 with PEO exhibit the same EL spectra with peaks at 608 nm, commission Internationale del'Eclairage (CIE) coordinates of (0.58, 0.39) and equally turn-on voltages, respectively. Meanwhile, the EL spectra of R1 and R2 show an obvious emission peak on 540 nm, which attributed to its relative low doping concentration in the
solution-processed devices. Notably, the R1 and R2 show maximum efficiencies of 11.4 and 21.9 cd A$^{-1}$ for CE, 10.2 and 16.7 lm W$^{-1}$ for PE, 6.9 and 13.1 % for EQE, respectively. Obviously, with the PEO aiding, the EQE of R2 is higher 1.9 times than that of R1. Besides, the EL stability of R1 and R2 were also assessed and show the LT$_{50}$ of 61 and 107 hours at luminance of 100 cd m$^{-2}$, respectively. These results once adequately demonstrate the superiority of our proposed strategy would not only improve the EL efficiency and stability of solution-processed TSCF-OLEDs, but also provide a new route for developing more efficient all-fluorescent solution-processed OLEDs.

![Graph](image1)

Figure 4. a) The TBRb-based solution-processed devices lifetime without PEO and with PEO; b) The DBP-based solution-processed devices lifetime without PEO and with PEO. All devices measured at initial luminance of 100 cd m$^{-2}$.

4. Conclusion

In this work, an efficient strategy was proposed to suppress the harmful Dexter energy transfer and ACQ effect by introducing a polymer material into TSCF system, achieving more efficiency and stability of all-fluorescent solution-processed OLEDs. To demonstrate the feasibility of our proposed strategy, the TBRb-based devices Y1 without PEO and Y2 with PEO were firstly fabricated and show the maximum EQE$_{max}$ of 3.7 % and 6.6 %, respectively. Meanwhile, the LT$_{50}$ of Y1 is 4.7 times higher than that of Y2 at initial luminance of 100 cd m$^{-2}$. Subsequently, another classical red emission DBP was employed as emitter to construct solution-processed TSCF-devices. As expected, The R1 without PEO and R2 with PEO display same EL spectra and maximum EQE$_{max}$ of 6.9 % and 13.1 %, respectively. The LT$_{50}$ of R1 is 1.75 times higher than that of R2 at initial luminance of 100 cd m$^{-2}$, respectively. These results fully demonstrate the superiority of such strategy and may shed more light on developing more efficient all-fluorescent solution-processed OLEDs.

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