

Carbazole-dendronized thermally activated delayed fluorescent molecules with small singlet-triplet gaps for solution-processed organic light-emitting diodes

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ABSTRACT

Based on a multi-carbazole encapsulation strategy, two novel solution-processable thermally activated delayed fluorescence (TADF) molecules, named 2,8-bis(2,7-bis(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)-9,9-dimethylacridin-10(9*H*)-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (**1CzAcDBTO**) and 2,8-bis(9,9-dimethyl-2,7-bis(3,3',6,6'-tetra-*tert*-butyl-9*H*-[9,3':6',9''-tercarbazol]-9'-yl)acridin-10(9*H*)-yl)dibenzo[*b,d*]thiophene 5,5-dioxide (**2CzAcDBTO**), were synthesized. Both compounds exhibit excellent thermal stability and a small energy gap between the lowest singlet and triplet state, i.e., 0.02 eV for **1CzAcDBTO** and 0.04 eV for **2CzAcDBTO**, respectively. Attributed to the more effective reverse intersystem crossing process, the molecule **2CzAcDBTO** as the neat emitter realized better electroluminescent performances. The simplified devices with the neat dendrimers as the emissive layers exhibit significant improvements of the external quantum efficiencies (EQEs) by factors of 19.5 and 22.5, respectively compared with the device incorporating the small molecular core AcDBTO. By blending an additional TADF sensitizer with the dendrimers in a common host, enormous enhancements of efficiency and luminance were realized, e.g., a maximum EQE of 7.9% and a maximum luminance of 16380 cd/m². Remarkably, the EQE remains as high as 7.4% at the high luminance of 1000 cd/m², revealing a negligible efficiency roll-off.

1. Introduction

Thermally activated delayed fluorescence (TADF) emitters as the third generation emitting materials in organic light-emitting diodes (OLEDs) have attracted great attention [1–9]. In 2011, Adachi's group reported the OLED based on a purely organic TADF emitter, which could utilize both singlet and triplet excitons for light emission by reverse intersystem-crossing (RISC) process [10]. Later on, tremendous efforts were devoted to improving performances of OLEDs based on TADF emitters. Nowadays, many TADF molecules have been reported and the external quantum efficiencies (EQEs) can be achieved beyond 30% which have outperformed those of conventional fluorescent OLEDs and are comparable with those of phosphorescent organic light-emitting diodes (PhOLEDs) [3]. Besides, many TADF molecules could also

be utilized as assistant dopants or hosts to sensitize emitting dopants for higher EQEs and enhanced operational stability [11–16].

However, most of highly efficient TADF-based OLEDs are fabricated by vacuum evaporation techniques which require complicated fabricating processes, high cost and precise engineering. In view of saving energy, developing simple and cost-effective solution-processed TADF-based OLEDs is extremely imperative [17]. What's more, solution-processed technology is more beneficial to achieve large-size OLEDs, which is now urgently demanded for commercial products. As far as solution-processed OLEDs are concerned, the emitting layer (EML) materials require good solubility and film-forming ability, which is at present a dominating challenge. Many reports have proposed effective strategies to acquire excellent organic materials for solution-processed OLED. One of the most notable solutions is multi-carbazole encapsulation strategy

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for developing dendrimers. As we all know, carbazole derivatives generally possess good hole-transporting ability, uniform film-forming properties and good thermal stability. Therefore, based on a multi-carbazole encapsulation strategy, a TADF core can be dendronized by carbazole units to construct solution-processed TADF dendrimers. For example, Luo et al. synthesized two greenish-blue emitters *via* the introduction of carbazole dendrons into the multi-positions of a TADF emissive core, achieving a peak EQE of 12.2% [18]. Pan et al. designed a self-host TADF dendrimer POCz-DPS for solution-processed non-doped blue OLED with the highest EQE of 7.3% [19]. Li et al. fabricated green OLEDs based on carbazole-dendronized TADF emitters formed by a solution process with a maximum EQE of 13.8% [20]. In general, the multi-carbazole encapsulation strategy to develop dendrimers is promising to achieve highly efficient solution-processed OLEDs [18–27].

However, for the multi-carbazole encapsulation strategy, choosing an appropriate emitter core is particularly crucial. The core should possess an extremely small gap between lowest singlet and triplet states (ΔE_{ST}) to guarantee efficient RISC process. In general, a pre-twisted donor-acceptor-donor (D-A-D) structure can spatially separate orbital overlap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) to achieve a small ΔE_{ST} . Therefore, we here chose 2,8-bis(9,9-dimethylacridin-10(9H)-yl)dibenzo[b,d]thiophene 5,5-dioxide (AcDBTO) as an emissive core [28], as shown in Fig. 1. Owing to steric hindrance effect, the compound AcDBTO acquires large twist angle between electron donor and acceptor units, which results in an extremely small ΔE_{ST} of 0.06 eV and distinct TADF features. Via decorating dendronized carbazole units, we have synthesized two new solution-processed TADF molecules, 2,8-bis(2,7-bis(3,6-di-*tert*-butyl-9H-carbazol-9-yl)-9,9-dimethylacridin-10(9H)-yl)dibenzo[b,d]thiophene 5,5-dioxide (1CzAcDBTO) and 2,8-bis(9,9-dimethyl-2,7-bis(3,3'',6,6''-tetra-*tert*-butyl-9'H-[9,3':6',9''-tercarbazol]-9'-yl)acridin-10(9H)-yl)dibenzo[b,d]thiophene 5,5-dioxide (2CzAcDBTO). Both compounds exhibit excellent thermal stability and small ΔE_{ST} s of 0.02 eV for 1CzAcDBTO and 0.04 eV for 2CzAcDBTO, respectively. The simplified devices with the neat dendrimers as the emissive layers exhibit significant improvements of the external quantum efficiencies (EQEs) by factors of 19.5 and 22.5, respectively compared with the device incorporating the small molecular core AcDBTO. Moreover, the spin-coated non-doped device based on 2CzAcDBTO achieved a maximum current efficiency (CE) of 13.9 cd/A and the electroluminescence (EL) peak wavelength at 538 nm. By blending a TADF sensitizer with the dendrimer in a common host, significant enhancements of the efficiency and the luminance were realized, e.g., a maximum EQE of 7.9% and a maximum luminance of 16380 cd/m², which were respectively twofold and fourfold of those of the non-doped device with 2CzAcDBTO. Remarkably, the EQE remains as high as 7.4% at the high luminance of 1000 cd/m², revealing an extremely small efficiency roll-off.

2. Experimental section

2.1. Synthesis and characterization

Scheme 1 shows the chemical structures and synthetic routes of the compounds 1CzAcDBTO and 2CzAcDBTO. The intermediate 4IAcDBTO was produced by *N*-iodosuccinimide (NIS) electrophilic substitution reaction with yield of 90%. Then the target compounds, 1CzAcDBTO and 2CzAcDBTO, were synthesized by Ullmann C-N coupling reaction between 4IAcDBTO and R₁H or R₂H, respectively. Chemical structures of new compounds were all characterized by ¹H NMR and ¹³C NMR spectroscopy, elemental analysis and mass spectrometry.

2.1.1. Synthesis of 4IAcDBTO

A mixture of AcDBTO (2.52 g, 4 mmol) and *N*-iodosuccinimide (3.60 g, 16 mmol) in 250 mL chloroform was stirred at 50 °C for 72 h in the dark. After cooling to room temperature, the reaction was quenched with a saturated aqueous solution of Na₂S₂O₃, the reaction mixture was extracted with dichloromethane, and dried with anhydrous Na₂SO₄. The production was purified by column chromatography (silica, dichloromethane/*n*-hexane 1:1 by volume) to give a green powder. Yield 90%. ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.15 (d, *J* = 8.0 Hz, 2H), 7.68 (s, 4H), 7.66 (s, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 4H), 6.01 (d, *J* = 8.8 Hz, 4H), 1.61 (s, 12H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 146.39, 139.34, 137.58, 135.48, 134.43, 134.18, 133.84, 132.69, 125.29, 124.61, 116.27, 84.46, 35.94, 31.16. MALDI-TOF (*m/z*): 1118.6 [M⁺ - CH₃]. Anal. calcd for C₄₂H₃₀I₄N₂O₂S (%): C, 44.47; H, 2.67; N, 2.47; O, 2.82. Found: C, 44.65; H, 2.78; N, 2.50.

2.1.2. Synthesis of 1CzAcDBTO

A mixture of R₁H (0.59 g, 2 mmol), 4IAcDBTO (1.13 g, 1 mmol), CuI (3.80 mg, 0.02 mmol), K₃PO₄ (4.24 g, 20 mmol), (±)-trans-1,2-cyclohexanediamine (3.42 mg, 0.03 mmol) and 1,4-dioxane (8 mL) was stirred at 110 °C under argon atmosphere for 48 h. After cooling to room temperature, the reaction was quenched with a saturated aqueous solution of NaCl. The reaction mixture was extracted with dichloromethane, and dried with anhydrous Na₂SO₄. The production was purified by column chromatography (silica, dichloromethane/*n*-hexane 1:1 by volume) to give a green powder. Yield 69%. ¹H NMR (400 MHz, CDCl₃, δ ppm): 8.28 (d, *J* = 8.0 Hz, 2H), 8.12 (s, 8H), 8.08 (s, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.66 (s, 4H), 7.43 (d, *J* = 8.8 Hz, 8H), 7.27 (d, *J* = 8.8 Hz, 8H), 7.21 (d, *J* = 8.4 Hz, 4H), 1.76 (s, 12H), 1.41 (s, 72H). ¹³C NMR (100 MHz, CDCl₃, δ ppm): 146.90, 142.61, 139.43, 138.54, 137.85, 134.69, 134.61, 131.90, 131.25, 125.42, 125.37, 125.32, 124.85, 123.56, 123.10, 116.30, 115.04, 108.93, 36.57, 34.71, 32.01, 31.58. MALDI-TOF (*m/z*): 1740.4 [M⁺]. Anal. calcd for C₁₂₂H₁₂₆N₆O₂S (%): C, 84.19; H, 7.30; N, 4.83; O, 1.84. Found: C, 83.92; H, 7.19; N, 4.76.

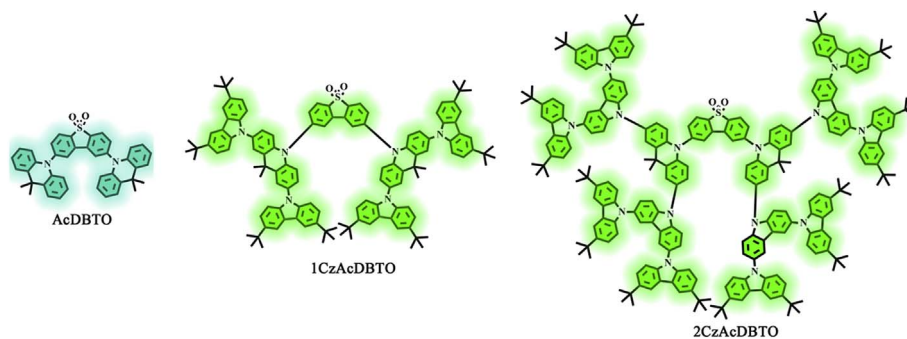


Fig. 1. Molecular structures of AcDBTO, 1CzAcDBTO and 2CzAcDBTO.

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