



Molecular design of deep blue fluorescent emitters with 20% external quantum efficiency and narrow emission spectrum



Inho Lee ^a, Jun Yeob Lee ^{b,*}

^a Department of Polymer Science and Engineering, Dankook University, 126, Jukjeon-dong, Suji-gu, Yongin, Gyeonggi, 448-701, Republic of Korea

^b School of Chemical Engineering, Sungkyunkwan University, 2066, Seobu-ro, Jangan-gu, Suwon, Gyeonggi, 440-746, Republic of Korea

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ABSTRACT

A thermally activated delayed fluorescent (TADF) emitter, 2,7-bis(9,9-dimethylacridin-10(9H)-yl)-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (DMTDAc), was developed as a deep blue TADF emitter using a rigid 9,9-dimethyl-9H-thioxanthene 10,10-dioxide (DMTD) acceptor and an acridine donor. The rigid DMTD acceptor narrowed emission spectrum of DMTDAc by interlocking two phenyl units of diphenylsulfone. A deep blue TADF device with an external quantum efficiency close to 20% with a deep blue color coordinate of (0.15,0.13) was provided using the DMTDAc TADF emitter.

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1. Introduction

Recently, the development of highly efficient blue devices has emerged as an issue because of high power consumption of full color organic light-emitting diode (OLED) panel caused by low efficiency of the blue devices. The use of fluorescent emitting materials in the blue pixel gave rise to increase of power consumption because of low quantum efficiency (QE) of the blue fluorescent emitters compared to phosphorescent red and green emitters. Therefore, there is a strong demand for the development of highly efficient blue emitters and OLEDs.

There have been mainly two approaches to develop the high efficiency blue OLEDs, which are phosphorescent OLEDs [1,2] and thermally activated delayed fluorescent OLEDs [3,4]. For the last 10 years, many host and dopant materials were synthesized for application in blue phosphorescent OLEDs, which upgraded the device performances of blue phosphorescent OLEDs [5–12]. The QE of the blue phosphorescent OLEDs is as high as 30% in sky blue device [5–8] and 25% in deep blue device [13]. However, the blue phosphorescent OLEDs have an intrinsic lifetime issue due to instability of the blue phosphorescent emitters [14]. The instability

of the blue triplet emitters motivated researchers to develop delayed fluorescent emitters which can reach the same QE level of the phosphorescent emitters and longer lifetime than the phosphorescent emitters. Basically, the molecular structure of the thermally activated delayed fluorescent (TADF) emitters consists of organic moieties which have an aromatic character and stabilize the chemical bond. Therefore, the blue TADF emitters gathered great attention and have been widely investigated for the last couple of years [3,4,15–20]. Recently, it was demonstrated that the blue TADF emitters can achieve 20% external QE (EQE) and longer lifetime than phosphorescent emitters in the blue devices [15]. However, there remain some problematic issues in the development of blue TADF devices, which are low efficiency in the deep blue device and broad electroluminescence (EL) spectra. Therefore, TADF emitters which can show deep blue EL spectra with a narrow full width at half maximum (FWHM) are need to overcome the hurdle of current blue TADF devices.

Herein, we propose a design strategy of deep blue emitting TADF emitter with a narrow FWHM by synthesizing a blue TADF emitter, 2,7-bis(9,9-dimethylacridin-10(9H)-yl)-9,9-dimethyl-9H-thioxanthene 10,10-dioxide (DMTDAc), with a rigid 9,9-dimethyl-9H-thioxanthene 10,10-dioxide (DMTD) acceptor and acridine donor. The bridged acceptor moiety, DMTD, narrowed the emission spectra of the blue TADF emitter and enabled the deep blue emission in the TADF device. A high EQE close to 20% with a deep blue

* Corresponding author.

E-mail address: leej17@skku.edu (J.Y. Lee).

color coordinate of (0.15,0.13) was provided using the DMTDAC TADF emitter. This work is the first development of deep blue TADF device with close to 20% EQE with x plus y value less than 0.30 in the color coordinate. The design strategy restricting the segmental motion of the backbone structure was a useful way of narrowing the EL spectra of the TADF devices.

2. Results and discussion

The design of DMTDAC was motivated by the molecular structure of DMAC-DPS which has a diphenylsulfone acceptor and an acridine donor [4]. The DMAC-DPS was verified to be a highly efficient blue TADF emitter by providing above 20% EQE in the blue device. However, the DMAC-DPS emitter could not reach a deep blue color coordinate and showed rather broad EL spectra, which are not suitable for applying DMAC-DPS in display application. As a method of resolving the broad spectrum issue of DMAC-DPS, a molecular design of replacing the diphenylsulfone core of DMAC-DPS with DMTD was adopted based on an idea that the interlocking of two phenyl units of diphenylsulfone would suppress vibrational motion and vibrational emission peak of the molecule.

Brominated DMTD which was prepared by bromination of 9H-thioxanthen-9-one followed by methylation and oxidation was an intermediate of the final DMTDAC TADF emitter. The two phenyl units connected to the central sulfone functional moiety were interlocked by the dimethyl substituted carbon linkage. The coupling reaction between the brominated DMTD and acridine yielded the DMTDAC emitter. Recrystallization, column chromatography and vacuum sublimation purified the final DMTDAC for chemical identification, photophysical characterization and device evaluation. Preparation of DMTDAC is schematically presented in Scheme 1.

The effect of interlocking of two phenyl units of DMTDAC was investigated by analyzing photoluminescence (PL) emission. Room temperature solution PL spectrum (fluorescence) from charge transfer (CT) excited state and low temperature PL emission spectrum (phosphorescence) obtained after applying delay time are displayed in Fig. 1. The delay time was applied to remove fluorescence from the low temperature PL spectrum. Both singlet and triplet energy of DMTDAC was 3.10 eV from the onset of solution PL and low temperature PL, respectively, and the singlet-triplet energy gap of DMTDAC was 0 eV. FWHM of DMTDAC from PL measurement was 61 nm, which was narrower than that of the well-known DMAC-DPS (67 nm). As explained in the molecular design concept, the interlocking of two phenyl units narrowed the PL emission peak. In addition, the origin of the solution PL emission was identified as CT emission from the solvatochromic effect.

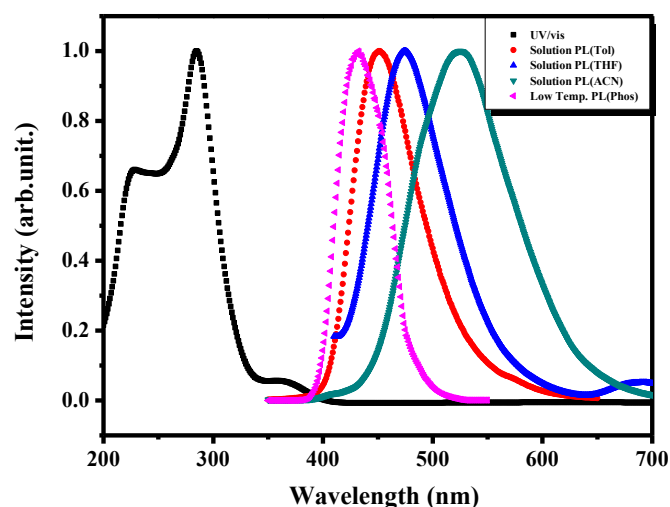
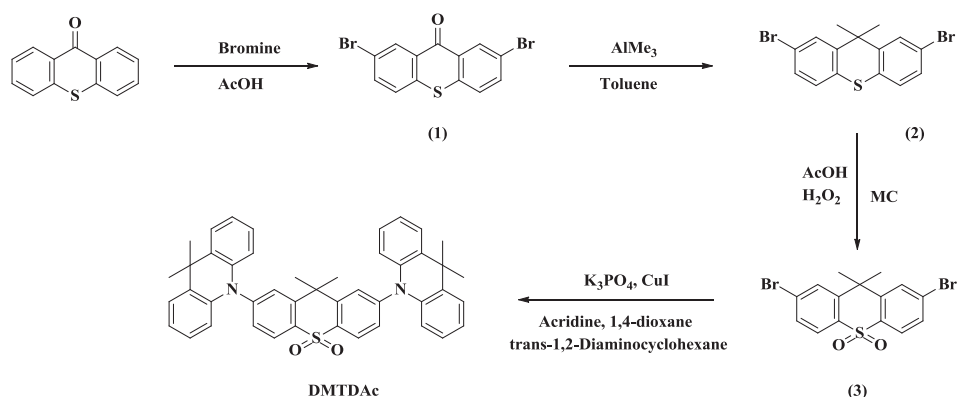


Fig. 1. UV-vis, solution PL and low temperature PL spectra in toluene of DMTDAC. Solvent dependent PL spectra in toluene, tetrahydrofuran and acetonitrile were also added.

Ultraviolet-visible (UV-vis) absorption investigation indicated that DMTDAC has strong π - π^* transition (200–350 nm) by molecular backbone structure and weak CT absorption (350–400 nm) by the acridine donor and DMTD acceptor. Absolute PL quantum yield of the DMTDAC dispersed in mixed host of 1,3-bis(triphenylsilyl)benzene (UGH3) and diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1) was 100% under nitrogen and it was 96% in air from integrating sphere measurement. It can be estimated from the PL quantum yield measurement results that all triplet excitons generated by intersystem crossing (4%) go back to singlet state by reverse intersystem crossing. Therefore, DMTDAC behaved as a TADF emitter fully harvesting triplet excitons.

The TADF character of DMTDAC was further verified by transient PL decay curve showing delayed fluorescence of the DMTDAC doped film. The transient PL decay curve in Fig. 2 demonstrated delayed emission of DMTDAC with an excited state lifetime of 1.2 μ s at room temperature. The small singlet-triplet energy gap of DMTDAC activated TADF emission with a short excited state lifetime. Increase of delayed fluorescence emission and fast PL decay at high temperature indirectly tells that the origin of the delayed fluorescence is TADF.

Although the interlocking of DMTDAC affected the PL emission behavior, electronic molecular orbital of DMTDAC was quite similar to that of DMAC-DPS. Well separation of the highest occupied



Scheme 1. Synthetic scheme of DMTDAC.

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