



Aggregation-induced emission type thermally activated delayed fluorescent materials for high efficiency in non-doped organic light-emitting diodes



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ABSTRACT

Aggregation-induced emission (AIE) type thermally activated delayed fluorescent (TADF) emitters were developed by asymmetric substitution of donor moieties to a diphenylsulfone acceptor. The AIE properties of the TADF emitters increased the quantum efficiency of the non-doped TADF devices and asymmetric substitution was more effective than symmetric substitution to enhance the quantum efficiency of the non-doped devices.

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1. Introduction

Organic light-emitting diodes (OLEDs) generally have a stack structure of a doped emitting layer sandwiched between charge transport layers. The doped emitting layer is essential in the construction of high efficiency OLEDs although device fabrication process of OLEDs becomes complicated by co-evaporation of host and dopant materials simultaneously. Therefore, it is desired to realize high efficiency using a non-doped emitting layer, but the development of high efficiency emitters and simple device structure has been a challenge among researchers in the field of OLEDs because intrinsic aggregation induced quenching of excitons in a non-doped emitting layer degrades the efficiency of OLEDs [1–10].

An approach to avoid the exciton quenching in a non-doped emitting layer was to utilize aggregation induced emission (AIE) behavior of fluorescent emitters [11,12]. The AIE characteristics were typically observed in the tetraphenylethene derivatives by restricted intramolecular rotation and could improve the quantum efficiency (QE) of non-doped devices. However, conventional fluorescent emission of the AIE type emitters can realize only 25%

internal QE and high external QE could not be reached using the tetraphenylethene type emitters [13–18].

Recently, it was demonstrated that delayed fluorescent type emitters such as thermally activated delayed fluorescent (TADF) emitters can be as efficient as phosphorescent emitters as all excitons can take part in the electroluminescence (EL) process [19–29]. Therefore, the best way to develop high efficiency non-doped fluorescent OLEDs is to design and apply AIE emitters with TADF characteristics [30].

In this work, symmetric and asymmetric AIE type emitters showing TADF behavior were synthesized and were evaluated as a non-doped emitting material in fluorescent OLEDs. An asymmetrically designed emitter, 10-(4-((4-(10H-phenothiazin-10-yl)phenyl)sulfonyl)phenyl)-10H-phenoxazine (PTSOPQ), behaved as both AIE and TADF emitters and achieved high external QE of 17.0% in a non-doped fluorescent OLEDs.

2. Experimental

2.1. General information

All reagents were purchased from commercial suppliers and used as received. All solvents were used without additional

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purification. General characterization of the synthesized compounds was conducted according to literature [31].

2.2. Synthesis

2.2.1. 10-(4-((4-fluorophenyl)sulfonyl)phenyl)-10H-phenothiazine (1)

A mixture of 10H-phenothiazine (3.00 g, 15.05 mmol) and sodium hydride (0.36 g, 15.05 mmol) in dimethylformamide (DMF) (50 mL) was stirred at room temperature for 30 min. After stirring, bis(4-fluorophenyl) sulfone (7.65 g, 30.11 mmol) in DMF was added, and then the mixture was stirred at 60 °C for 1 h followed by cooling to room temperature. The solution was extracted with dichloromethane (MC) and then the solvent was removed under vacuum. The resulting product was purified over silica gel with ethyl acetate/n-hexane as the eluent.

Yield: 4.9 g (76.6%), ¹H NMR (400 MHz, d-DMSO): δ 7.98–7.95 (m, 2H, J = 7.2 Hz), 7.82 (d, 2H, J = 4.4 Hz), 7.53 (d, 2H, J = 4.4 Hz), 7.43 (t, 2H, J = 8.8 Hz), 7.39–7.34 (m, 4H, J = 8.8 Hz), 7.27 (t, 2H, J = 8.4 Hz), 7.1 (d, 2H, J = 6 Hz). ¹³C NMR (100 MHz, d-DMSO): δ 166.4, 163.9, 149.6, 140.9, 138.8, 133.2, 132.5, 130.8, 130.7, 129.9, 129.3, 128.5, 127.1, 126.7, 117.5, 117.3, 116.9. MS(APCI) 434 m/z.

2.2.2. 10,10'-(sulfonylbis(4,1-phenylene))bis(10H-phenothiazine) (PTSOPT)

A mixture of 10H-phenothiazine (1.57 g, 7.87 mmol) and sodium hydride (0.38 g, 15.73 mmol) in dimethylformamide (DMF) (30 mL) was stirred at room temperature for 30 min. After stirring, bis(4-fluorophenyl) sulfone (1.00 g, 3.93 mmol) in DMF was added, and then the mixture was stirred at 60 °C for 1 h followed by cooling to room temperature. The solution was extracted with dichloromethane (MC) and then the solvent was removed under vacuum. The resulting product was purified over silica gel with ethyl acetate/n-hexane as the eluent.

Yield: 1.8 g (74.7%), ¹H NMR (400 MHz, d-DMSO): δ 7.78 (d, 4H, J = 7.2 Hz), 7.51 (d, 4H, J = 4.2 Hz), 7.37 (t, 4H, J = 8.4 Hz), 7.3 (d, 4H, J = 4.2 Hz), 7.26 (t, 4H, J = 8.2 Hz), 7.11 (d, 4H, J = 7.2 Hz). ¹³C NMR (400 MHz, d-DMSO): δ 149, 141.2, 134.7, 131.8, 129.7, 129.2, 128.4, 126.8, 126.1, 117.8. MS(APCI) 613 m/z.

2.2.3. 10-(4-((4-(10H-phenothiazin-10-yl)phenyl)sulfonyl)phenyl)-10H-phenoxazine (PTSOPO)

A mixture of 10H-phenoxazine (0.37 g, 2.03 mmol) and sodium hydride (0.05 g, 2.03 mmol) in DMF (30 mL) was stirred at room temperature for 30 min. After that, (1) (0.80 g, 1.85 mmol) in DMF was added, and then the mixture was stirred at 60 °C for 1 h. After cooling, the solution was extracted with dichloromethane (MC), and then the solvent was removed in vacuo. The resulting product was purified over silica gel with ethyl acetate/n-hexane as the

eluent and then sublimed in vacuum.

Yield: 0.54 g (49%), ¹H NMR (400 MHz, d-DMSO): δ 8.1 (d, 2H, J = 4 Hz), 7.85 (d, 2H, J = 4 Hz), 7.64 (d, 2H, J = 6 Hz), 7.55 (d, 2H, J = 4 Hz), 7.45 (d, 2H, J = 4 Hz), 7.4 (t, 2H, J = 8 Hz), 7.28 (t, 2H, J = 4 Hz), 7.1 (d, 2H, J = 6 Hz), 6.7 (d, 2H, J = 6 Hz), 6.68 (t, 2H, J = 8 Hz), 6.6 (t, 2H, J = 10 Hz), 5.86 (d, 2H, J = 4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 150.1, 144.1, 143.6, 142.4, 140.8, 134.2, 133.5, 132, 131.7, 130.2, 129.8, 129.1, 127.6, 126.8, 126.6, 123.4, 122.2, 115.9, 115.3, 113.5. MS (FAB) m/z: 596 [(M + H)⁺].

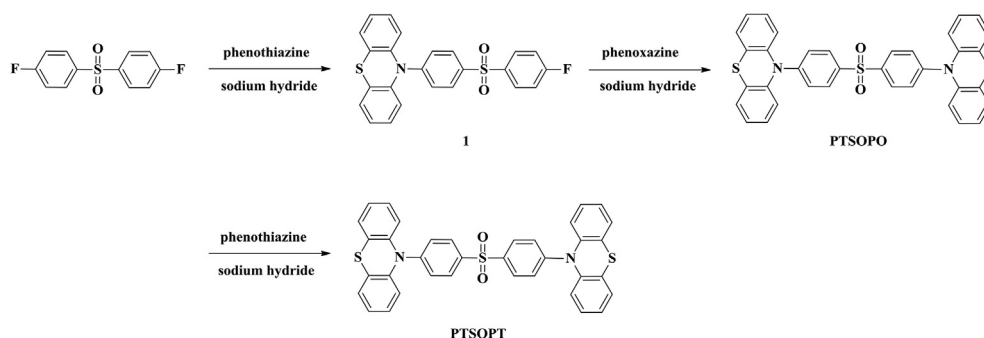
2.3. Device fabrication and measurements

The PTSOPO emitter was evaluated in the device structure of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) (60 nm)/4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)aniline] (TAPC) (20 nm)/1,3-bis(N-carbazolyl)benzene (mCP) (10 nm)/bis[2-(diphenylphosphino)phenyl] ether oxide (DPEPO):PTSOPO or PTSOPO (25 nm)/diphenylphosphine oxide-4-(triphenylsilyl)phenyl (TSPO1) (5 nm)/1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBI) (30 nm)/LiF (1 nm)/Al (200 nm). 10,10'-(Sulfonylbis(4,1-phenylene))bis(10H-phenothiazine) (PTSOPT) was also tested in the same device structure. All devices were optically and electrically tested after encapsulating all devices using CS 2000 spectroradiometer and Keithley 2400.

3. Results and discussion

The asymmetric AIE emitter, PTSOPO, was prepared by stepwise substitution of phenothiazine and phenoxazine to a bis(4-fluorophenyl) sulfone acceptor by controlling molar ratio of phenothiazine to 0.5 equivalent of bis(4-fluorophenyl) sulfone. Isolation of mono substituted 10-(4-((4-fluorophenyl)sulfonyl)phenyl)-10H-phenothiazine and subsequent reaction with phenoxazine provided the PTSOPO as a final product. Final production yield of PTSOPO was 49% after purifying the product by wet and sublimation purification. Chemical identification of PTSOPO was conducted after final purification. Synthetic procedure of PTSOPO and PTSOPT is simply depicted in Scheme 1.

Basic photophysical characterization data of PTSOPO were collected by monitoring ultraviolet–visible (UV–vis) and photoluminescence (PL) measurement results in Fig. 1. The UV–vis spectrum of PTSOPO displayed main absorption peaks by the phenothiazine and phenoxazine substituted diphenylsulfone backbone structure and very weak absorption peaks from 375 nm to 419 nm which are assigned to charge transfer (CT) absorption by donor–acceptor structure of PTSOPO. PL emission at room temperature and low temperature was studied using toluene solution. PL emission edge and low temperature PL emission edge of PTSOPO were 418 nm and 431 nm, respectively. As the origin of the PL



Scheme 1. Synthetic route of PTSOPO and PTSOPT.

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