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A bipolar macrospirocyclic oligomer based on triphenylamine and 4,5-diazafluorene as a solution-processable host for blue phosphorescent organic light-emitting diodes

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ABSTRACT

A bipolar macrospirocyclic trimer based on 4,5-diazafluorene and triphenylamine was prepared as a host for solution-processed blue phosphorescent organic light emitting diodes. The oligomer exhibits a high triplet energy of 2.88 eV, excellent thermal and morphological stability, good film-forming ability and solution processability. A solution-processed phosphorescent device based on FIrpic and the trimer achieved a maximum current efficiency of 10.0 cd A^{-1} with a low current efficiency roll-off at the practical luminance (9.6, 10.0, 9.4 cd A^{-1} at 102, 207, 1096 cd m^{-2}, respectively). The oligomer additionally showed excellent chemical compatibility with the common host for solution-processing technology. A blue phosphorescent device using mixed hosts of the trimer/4,4′-cyclohexylidenebis(*N*,*N*-bis(4-methyl -phenyl)benzenamine) achieved a low turn-on voltage of 3.0 V, a maximum luminance of 28,368 cd m^{-2}, and a maximum current efficiency of 17.7 cd A^{-1} (11.9 lm W^{-1}), which is almost three times that of a single 4,4′-cyclohexylidenebis(*N*,*N*- bis(4-methylphenyl)benzenamine)-hosted device.

1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) continue to attract much research attention, because they can harvest both singlet and triplet excitons to realize up to 100% internal quantum efficiency [1–5]. To achieve efficient PhOLEDs with low efficiency roll-off and extended operational lifetime, several requirements need to be considered in the search for efficient host materials [6,7], such as higher triplet energy (E_T) than that of the guest, matched highest occupied molecular orbital (HOMO)/lowest unoccupied molecular orbital (LUMO) energy level, good thermal stability and film-forming ability. Balanced carrier transport properties of hosts are also favored to improve device efficiency and reduce efficiency roll-off. An effective way to balance carrier transport is to configure bipolar hosts [8–11] with electron donor and acceptor groups, since they can transport holes and electrons simultaneously to broaden the recombination region within the emitting layer, thereby improving device efficiency. Most of the reported bipolar hosts were designed to possess a given ratio of donor to acceptor units, which may impede device performance as perfect charge balance was hardly achieved [12,13]. An alternative strategy involves the use of mixed hosts [14–17], for convenient manipulation of charge transport properties can be achieved by tuning the composition of the mixed hosts. Furthermore, the aggregation in the mixed hosts can be suppressed because the intermixing of the host materials hinders the molecular packing of

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each individual host material, which promises stable amorphous films. However, the host materials for the mixed-host system should be carefully chosen because some host materials are immiscible (or form an exciplex) and suffer from phase separation in the film state upon heating, especially in solution-processed PhOLEDs [18,19].

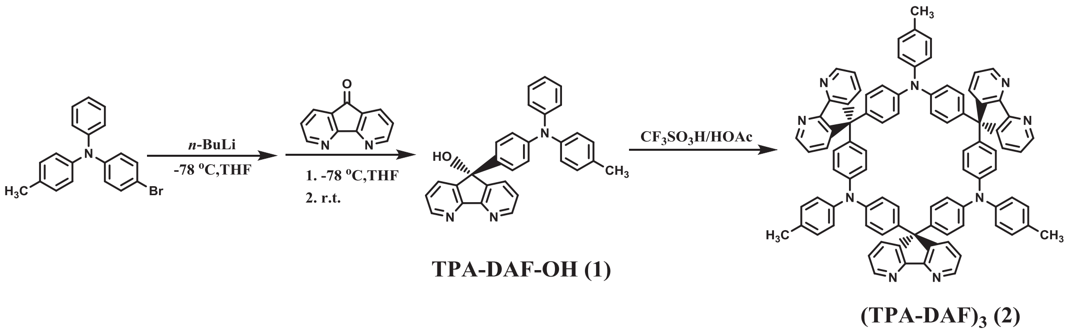
On the other hand, solution-processability of host materials is considered critical to realize low-cost and large-area displays compared with vacuum deposition [20,21]. Recently, apart from polymers [22,23] and some small molecules [13,24], monodisperse oligomers [25–27] have been realized as a new class of efficient host materials for solution-processed PhOLEDs, for they combine the advantages of special characteristics including controllable molecular structures, ease of purification, characterization, and solution-processability. Macrocyclic oligomers, which represent a class of infinite polymer chains without any end groups from a fundamental standpoint, are very attractive for optoelectronic applications as they also comprise discrete, monodisperse structures [28,29]. In such macrocyclic molecules, the chemically active sites can be blocked, so that desirable merits such as high electrochemical stability is anticipated. Most of above oligomers are designed as unipolar host materials. Previously, we also successfully constructed two monodisperse oligomers based on triphenylamine/fluorene for blue solution-processed PhOLEDs through a simple Friedel-Crafts condensation reaction [30,31]. In this paper, we further presented a novel bipolar oligomer derived from triphenylamine (TPA) and 4,5-diazafluorene (DAF) as a solution-processable host. Herein, 4,5-diazafluorene contains two fused pyridine rings, which endows it with reasonably strong electron affinity and makes it a good electron acceptor for constructing bipolar hosts [32–36]. In the produced oligomer (TPA-DAF)$_3$, TPA and DAF units are connected in series through *para*-Cs of TPA and the C-9s of DAF (Scheme 1), so that the conjugation length of each individual building block should essentially remain unperturbed, imparting (TPA-DAF)$_3$ a high E_T of 2.88 eV to host the triplet emitter iridium(III) bis[(4,6-difluorophenyl)-pyridinato-*N,C*^{2}] picolinate (FIrpic). (TPA-DAF)$_3$ exhibited excellent thermal stability, film-forming ability, and compatibility with FIrpic. Solution-processed blue PhOLED with the configuration of ITO/PEDOT: PSS (25 nm)/(TPA-DAF)$_3$: 15 wt% FIrpic (35 nm)/TPBI (35 nm)/Ca (10 nm)/Ag achieved a maximum current efficiency of 10.0 cd A^{-1} with a low efficiency roll-off at practical luminance (9.6 cd A^{-1} at 102 cd m^{-2} and 9.4 cd A^{-1} at 1096 cd m^{-2}). Furthermore, (TPA-DAF)$_3$ showed excellent doping capability with the common host TAPC (*N,N*-bis(4-methylphenyl)- benzenamine) in solution procedure. The blue PhOLEDs with the structure of ITO/PEDOT: PSS (25 nm)/[(TPA-DAF)$_3$: TAPC = 3:7]: 15 wt% FIrpic (35 nm)/TPBI (35 nm)/Ca (10 nm)/Ag showed a maximum current efficiency of 17.7 cd A^{-1} and a maximum luminance of 28368 cd m^{-2}, with a low turn-on voltage of 3.0 V (see Table S1).

2. Experimental

2.1. Materials and methods

4-Bromo-*N*-phenyl-*N*-(*p*-tolyl)aniline was prepared using the method reported in the literature [37]. 4,5-Diazafluoren-9-one was purchased from Alfa Chemistry. Other chemicals and solvents were purchased from commercial sources and used as received except where noted.

^{1}H NMR, ^{13}C NMR spectra were recorded in CDCl$_3$ on a 500 MHz spectrometer (Bruker Daltonics, Germany). ^{1}H NMR chemical shifts (δ) were referenced to tetramethylsilane (TMS), and ^{13}C NMR chemical shifts (δ) were referenced to internal solvent resonance. IR spectra were recorded on a Nexus 870 FTIR spectrophotometer (Bruker) using KBr pellets. The melting points of the samples were measured with the SGW X-4A melting point apparatus (Shen-Guang, China). UV–vis absorption spectrum at room temperature was obtained on a Lambda 35 spectrophotometer (PerkinElmer). Fluorescence spectrum at room temperature was measured with a LS-55 fluorescence spectrometer (PerkinElmer). Atomic force microscopy (AFM) measurements were carried out on Bruker Nano Surfaces instrument. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Instrument (Pyris 1 TGA). The thermal stability of the sample was determined by measuring the weight loss while heating at a rate of 20 °C min^{-1} from 50 to 750 °C under nitrogen atmosphere. Differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} from 50 to 300 °C was performed using a PerkinElmer Instrument (Pyris 1 DSC) under argon atmosphere. Positive-ion MALDI-TOF mass spectrometry was performed on an Autoflex II TOF/TOF time-flight mass spectrometer (Bruker Daltonics, Germany). Briefly, 0.5 mg of the sample was dissolved in 0.5 mL tetrahydrofuran, and then the sample solution (0.5 mL) was mixed with 0.05 mL of the matrix solution (50% acetonitrile with 0.5% trifluoroacetic acid solution saturated with cinnamic acid). Diluted solution (1 μL) was placed on the concave flat surfaces of a stainless steel plate and then air-dried. The spectra were obtained using reflector mode, and ions generated by a pulsed laser beam (nitrogen laser $\lambda = 337$ nm, 25 Hz) were accelerated to 19.0 kV with a delayed extraction (180 ns). The mass was analyzed by Flex-Analysis (Ver. 2.4, Bruker Daltonics, Germany). The Agilent 6540 high resolution mass spectrometer (HRMS) was employed for mass characterization. Cyclic voltammetry was carried out on a CHI600 electrochemical analyzer (Chenhua, Shanghai, China) at room temperature in a conventional three-electrode cell consisting of a glassy carbon as working electrode, a platinum wire as counter electrode, and an Ag/AgCl reference electrode. Nitrogen-purged dichloromethane (oxidation) and tetrahydrofuran (reduction)



Scheme 1. Synthetic route to (TPA-DAF)$_3$.