

The effect of carrier injection and transport of hosts on organic electrophosphorescent device

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ABSTRACT

Recently the organic electrophosphorescent host materials have attracted increasing attention. The selection principle of suited host materials is important to obtain high efficient electrophosphorescence. In this paper, we report the effect of carrier injection and transport properties of hosts to organic electrophosphorescent devices. A system, consisting of a red phosphorescent $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ dopant and two blue-emitting hosts THPH and TCPC introducing carbazole substituent groups, was studied. Both the hosts showed similar electronic properties, forming film ability and energy transfer degree to dopant, however, EL efficiency with TCPC host significantly exceeds that with THPH host. The Cyclic Voltammogram curves and single carrier devices of hosts TCPC and THPH show that TCPC with carbazole groups possesses stronger hole injection and transport ability, and this induced TCPC is more suited host than THPH. This result demonstrates our previous study that the electrochemical properties of dopant $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ molecule, which reflects the carrier trapping ability of guest, may be a basic design criterion for the selection of host.

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1. Introduction

Organic light-emitting diodes (OLEDs) have attracted great interest because of their potential applications in flat-panel displays [1–6]. Utilizing triplet-based emitting centers in OLEDs, and thereby capturing both singlet and triplet excited states, the internal quantum efficiency can, in principle, be 100% [7–12]. In phosphorescent devices, to reduce the quenching associated with relatively long excited-state lifetimes of triplet emitters and triplet–triplet annihilation, the phosphorescent emitters as emitting dopant guest are normally dispersed in a conductive organic/polymer host matrix [13–18]. Effective host materials are thus of equal importance for efficient phosphorescent OLEDs, and recently have attracted increasing attention.

Various types of host materials, including hole-transport-type [19–21], electron-transport-type [22–24] and bipolar transport-type [25–27] were designed and utilized for phosphorescent guest instead of conventional host materials, e.g. poly(vinylcarbazole) (PVK) [28–32], 4,4'-bis(9-carbazolyl)-2,2'-biphenyl (CBP) [19,33,34]. To be an effective host of the

phosphorescent guest three key factors must be considered together. Firstly, the host should possess an amorphous film morphology to ensure the device reproducibility and stability [35]. Secondly, the triplet energy of the host is required to be higher than guest in order to prevent the back energy transfer from the guest to the host [36]. Finally, the capability of the host to transport both holes and electrons to maintain the charge balance in the emissive layer so as to improve the device efficiency [37,38].

In our previous research we have presented a viewpoint about matching of phosphorescent guest and organic/polymer host that the electrochemical properties of phosphorescent molecules, which reflect their carrier trapping ability, may be a basic design criterion for the selection of host, due to multi-electroreduction processes and single electrooxidation process the hole-transfer host material is suitable to avoid radiationless deactivation [39]. However, further studies are still necessary to explore basic criterion for the selection of host.

In this paper, we employed both organic small molecular fluorene-based materials TCPC and THPH as host, which have similar molecular structure, difference in them is added carbazole groups at end of alkyl chains in TCPC. The TCPC and THPH have similar absorption and photoluminescence properties, and their thin films doped dopant by spin-coating possess high quality. Devices with TCPC host bearing carbazole-substituents were shown to possess a larger efficiency compared to similar devices utilizing THPH

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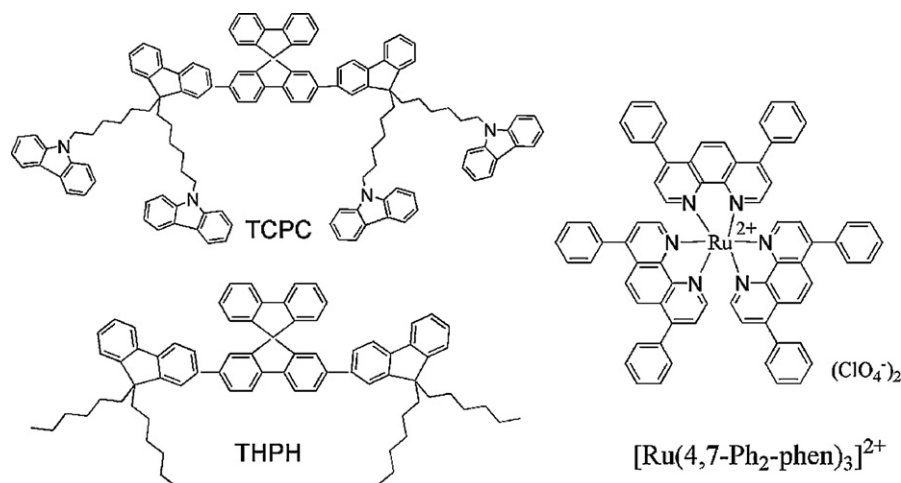


Fig. 1. Molecular structures of TCPC, THPH and $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$.

host. This improvement was attributed to more hole injection and transport of carbazole-substituted TCPC as host, leading to the matching with the electrochemical behavior of guest $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$.

2. Experimental

2.1. Materials and methods

The synthesis of $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ was reported elsewhere [40]. The PVK, PBD and TPD were purchased from Aldrich and used without further purification. The TCPC and THPH were synthesized by our laboratory. UV–vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. The films for PL experiments were prepared on pre-cleaned quartz plate in an air atmosphere.

Electrochemical measurements were performed with a BAS 100W Bioanalytical Systems, using a platinum disk ($\varphi=2\text{ mm}$) as working electrode, platinum wire as auxiliary electrode, with porous glass wick Ag/Ag^+ as reference electrode. Cyclic Voltammogram (CV) studies of the $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ were carried out at a scan rate of 50 mV/s and in DMF solutions containing 0.1 M NBu_4BF_4 as supporting electrolyte. CV studies of the TCPC and THPH solid film were carried out at a scan rate of 50 mV/s and in acetonitrile solutions containing 0.1 M NBu_4PF_6 as supporting electrolyte. Using the onset potentials in CV curve, the LUMO and HOMO energy levels of the material were determined; and using the difference between and LUMO and HOMO, the energy gap of the materials was estimated.

2.2. Device fabrication

Indium–tin-oxide (ITO) coated glass with a sheet resistance of $<50\ \Omega\text{ M}^{-1}$ was used as substrate. The substrate was pre-patterned by photolithography to give an effective device size of 4 mm^2 . Active layers were spin-coated from 5 mg/ml chloroform solutions of $0.5\text{--}8.0\text{ wt}\%$ $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ by weight in TCPC, THPH, TCPC-PBD (40 wt%), and THPH-TPD (20 wt%) at a speed of 3000 r/m on ITO substrates to give film thickness of $80\text{--}100\text{ nm}$. The cathode Ba (5 nm)/ Al (340 nm) was thermally deposited under vacuum pressure of $5 \times 10^{-4}\text{ Pa}$. For single-carrier devices active layers were spin-coated from 5 mg/ml chloroform solutions of TCPC or THPH, and Al (100 nm), Au (100 nm), or Ba (5 nm)/ Al (340 nm) was thermally deposited under vacuum pressure of $5 \times 10^{-4}\text{ Pa}$. The Luminance–current density–voltage characteristics were recorded

by combining the PR650 spectroscan spectrometer with a Keithley model 2400 programmable voltage–current source. The Electroluminescent (EL) spectra and Commission Internationale De L'Eclairage (CIE) coordination of devices are measured by the PR650 spectroscan spectrometer. These measurements were made at room temperature and ambient conditions.

3. Results and discussion

Fig. 1 shows molecular structures of host TCPC, THPH and $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$. The backbone of 9,9'-spirobifluorene-bridged bi(9,9'-bialkylfluorene)s of TCPC and THPH is same, the difference in them is added carbazole groups at end of alkyl chains in TCPC. Among various host materials reported, fluorene-based polymers and compounds as host matrix have attracted wide interest in recent years [41–48]. The introduction of spiro-configuration in fluorene-based materials gives the molecules a steric and bulky structure that further hinders interchromophore packing and enhances thermal and morphological stabilities and retains high photoluminescent quantum yields [47,48]. Our previous studies found that TCPC and THPH exhibit some intriguing properties [49]. Fig. 2 shows the absorption and photoluminescence (PL) spectra of TCPC, THPH and $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$. Both TCPC and THPH exhibit very similar spectroscopic properties: nearly the same lowest-energy absorption bands around 350 nm , similar PL spectra

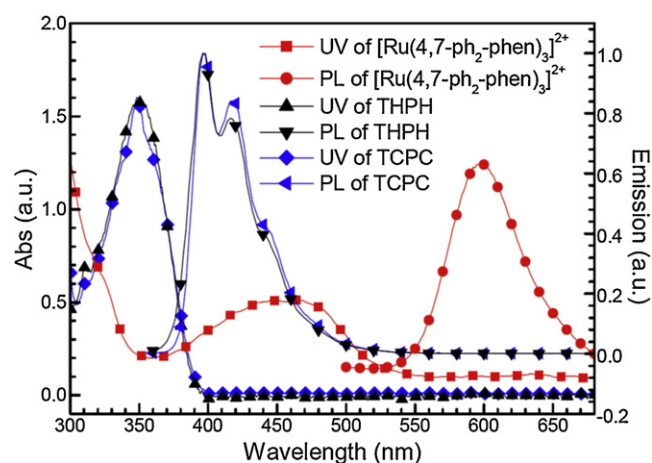


Fig. 2. Normalized spectra of absorption and emission of TCPC, THPH and $[\text{Ru}(4,7\text{-Ph}_2\text{-phen})_3]^{2+}$ (in CHCl_3).

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