New Thermally Cross-Linkable Polymer and Its Application as a Hole-Transporting Layer for Solution Processed Multilayer Organic Light Emitting Diodes

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A new thermally cross-linkable copolymer containing reactive benzocyclobutene (BCB) units and the well-known hole-transporting moiety *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine) (TPD) was synthesized and characterized. Thermal annealing of spun-cast films of the copolymer, followed by cross-linking at 200 °C, led to insoluble polymer films with a smooth surface. Green emitting fluorescent OLEDs were fabricated using the new cross-linkable polymer and compared with conventionally prepared devices. Using the thermally cross-linked copolymer as a hole-transporting layer, solution processed multilayer light emitting diodes were prepared that exhibited high performance with 10.4% external quantum efficiency at a brightness of 350 cd/m^2.

Introduction

Organic Light Emitting Diodes (OLEDs) have attracted much research interest in the last few decades due to their promising applications in full color displays and solid-state lighting.[1−8] The most efficient devices reported to date have been multilayer structures with heavy metal phosphorescent emitters, in which the hole-transporting layer (HTL), phosphorescent emitting layer (EL), and electron-transporting layer (ETL) are sandwiched between two electrodes. The advantages of a multilayer structure include facilitated charge carrier injection through reducing the respective injection barriers, enhanced recombination of electrons and holes in the EL, and decreased exciton quenching by the electrodes. The use of phosphorescent materials enables harvesting both singlet and triplet excitons leading to a theoretical internal quantum efficiency of 100%.[4,6,9] Device fabrication is usually carried out using one of two methods: high vacuum vapor deposition of small molecules or solution processing of polymers or dendrimers. For small molecules, multilayer structures are constructed through layer-by-layer vapor deposition, a very successful technique that is however limited to thermally stable low-molecular-weight materials and is relatively expensive and time-consuming. While fabrication of devices from solution using macromolecules would be an attractive alternative, the process is nontrivial, and one particular requirement for the deposition of multiple layers is that each deposited layer be resistant to the solvent used to deposit subsequent layers.[10]

Several strategies have been developed to overcome the dissolution issues associated with the solution processing of multilayer structures. A simple approach uses materials soluble in orthogonal solvent systems for each individual layer; for example, water soluble poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) PEDOT-PSS as HTL[5,11,12] may be followed by an organic soluble polymer as EL and finally by a water soluble copolymer as ETL.[13] Another general method that involves a liquid buffer layer has also been reported for the preparation of multilayer structures.[14] Perhaps the most elegant strategy involves the development of cross-linkable materials, which can be

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solution processed by spin casting or ink jet printing and then transformed into an insoluble film by light or heat treatment.[7,10,15−35] To date, most of the reported thermally cross-linkable hole-transport materials are based on the perfluorocyclobutane (PFCB) cross-linking unit.[30−34] Herein, we introduce a novel thermally cross-linkable hole-transporting polymer for solution processible multilayer OLEDs. This copolymer contains a benzocyclobutene (BCB) thermally reactive functional group as well as a *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD) hole-transporting moiety.[36] The synthesis and characterization of this novel copolymer as well as its early demonstration as a hole-transporting material in OLEDs are presented in this article.

Experimental Section

Synthesis of 4-[*N*-(4-Vinylphenyl)-*N*-(4-methylphenyl)amino]-4′-[*N*-phenyl-*N*-(4-methylphenyl)amino]biphenyl: 3.35 g (9.36 mmol). Methyl triphenylphosphonium bromide was dissolved in THF under an inert atmosphere. The solution was cooled to −78 °C, and 3.44 mL of a 2.5 M solution of n-BuLi in hexanes was added slowly. The mixture was then allowed to warm to room temperature and was stirred for 1 h before cooling again to −78 °C, and 4.23 g (7.77 mmol) of 4-[*N*-(4-formylphenyl)-*N*-(4-methylphenyl)amino]-4′-[*N*-phenyl-*N*-(4-methylphenyl)amino]biphenyl dissolved in THF was added slowly. The reaction mixture was allowed to warm to room temperature and stirred for 11 h at ambient temperature. Water was added to the reaction mixture, and the phases were separated; the organic phase was washed with water and brine and dried over $MgSO_4$, and the solvent was evaporated in vacuo. Column chromatography with a hexanes/ethyl acetate (9:1) solvent mixture yields 3.28 g (78%) of the product as a solid. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$ (dd, 4H, $J = 8.5$, 1.9 Hz), 7.34−7.22 (m, 5H), 7.15−7.04 (m, 16H), 7.01 (t, 1H, $J = 7.4$ Hz), 6.68 (dd, 1H, $J = 17.6$, 10.9 Hz), 5.60 (d, 1H, $J = 17.6$ Hz), 5.17 (d, 1H, $J = 10.9$ Hz), 2.35, (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 147.86$, 147.50, 146.88, 146.53, 145.09, 144.85, 136.23, 134.66, 134.27, 133.09, 132.87, 131.54, 129.99, 129.95, 129.15, 127.19, 127.00, 125.12, 125.02, 123.83, 123.75, 123.50, 123.17, 122.36, 111.94, 20.85. MS (EI) *m*/*z*: 543 (M^+, 6), 542 (13), 495 (10), 494 (21), 216 (17), 156 (6), 137 (39), 121 (100), 109 (8), 91 (10). HRMS($C_{40}H_{34}N_2$): calc. 542.2722; found: 542.2726. CHN Analysis (%) - calcd: C, 88.52; H, 6.31; N, 5.16; observed: C, 88.32; H, 6.67; N, 4.97.

Synthesis of TPD−BCB Copolymer. The monomers vinyl-TPD (0.541 g, 1.0 mmol), vinyl-BCB (13.02 mg, 0.1 mmol), and then free radical initiator AIBN (1.64 mg, 0.01 mmol) were dissolved in 1.0 mL of dry benzene in a 5 mL drying ampule. The polymerization mixture was degassed via three freeze−pump−thaw cycles and refilled with Ar. The ampule was sealed under Ar and heated to 60 °C for 24 h. The resulting polymer was dissolved in CH_2Cl_2 and precipitated into hexanes. After drying under vacuum, the TPD−BCB copolymer was obtained as a white powder: (0.47 g, 86%). ^{1}H NMR 6.55−7.29 (m, ArH), 3.10 (br, -CH_2CH_2-), 2.20 (br, -CH_3), 2.05 (br, -CH-) 1.53 (br, -CH_2-). CHN Analysis (%) - calcd: C, 88.62; H, 6.35; N, 5.03; observed: C, 88.29; H, 6.50; N, 4.86.

Devices Fabrication and Measurement. Indium tin oxide (ITO)-coated glass substrates were sequentially cleaned by sonication in soap solution; rinsed with deionized water; boiled in trichloroethylene, acetone, and ethanol for 5 min each; and dried with nitrogen. Finally, the substrates were treated with UV ozone for 10 min. For bilayer fluorescent devices, the polymers were dissolved in chloroform at a concentration of 10 mg/mL. The resulting solutions were filtered (0.2 μm poly(vinylidene difluoride) filter) prior to use. The solutions were spin-cast at 3000 rpm for 60 s. A 40 nm thick layer of AlQ_3 was deposited by thermal evaporation from resistively heated tantalum boats onto the polymer-coated substrates at a rate of 2.0 Å/s. The base pressure at room temperature was $(3-4) \times 10^{-6}$ Torr. For the multilayer phosphorescent devices, a solution of 36 mg/mL polymer with 8 wt % of green emitting iridium complexes in chlorobenzene was spin coated on the top of the cross-linked layer and ITO surface at 3000 rpm for 60 s. The thickness was about 80 nm. A 40 nm thick layer of BCP was then deposited at the same condition as for AlQ_3. After organic film deposition, the chamber was vented, and a shadow mask with a 2 mm wide stripe was put onto the substrates perpendicular to the ITO stripes. A cathode consisting of 1 nm LiF and 100 nm aluminum was deposited at a rate of 0.02 Å/s and 4−5 Å/s, respectively. OLEDs were formed at the 2×2 mm squares where the ITO (anode) and Al (cathode) stripes intersect.

The devices were tested in air within 2 h of fabrication. The electrical and optical intensity characteristics of the devices were measured with a Keithly 2400 sourcemeter/2000 multimeter coupled to a Newport 1835-C optical meter, equipped with a UV-818 Si photodetector. Only light emitting from the front face of the device

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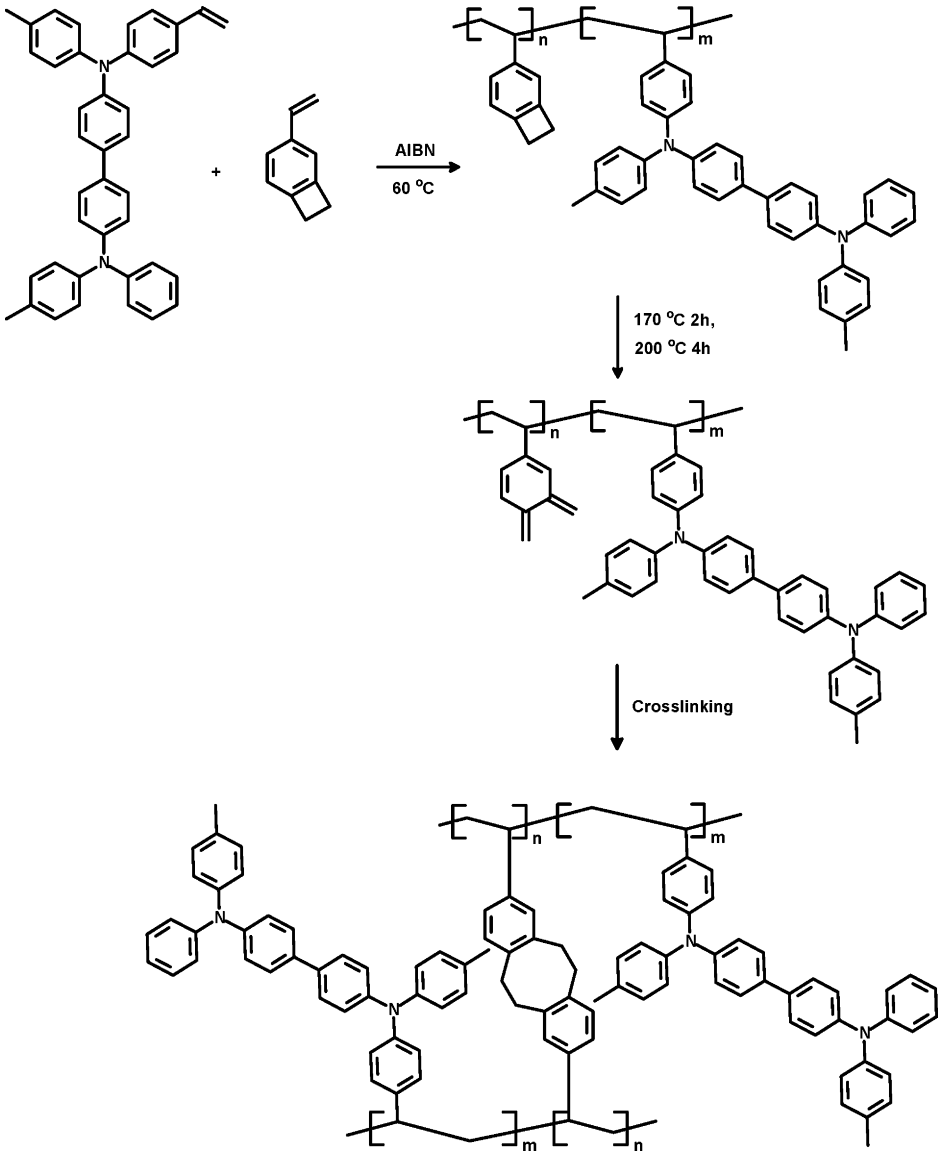
Scheme 1. Synthesis and Primary Cross-Linking Reaction of the TPD−BCB Copolymer



was collected and used in subsequent efficiency calculations. The electroluminescence (EL) spectra were measured on a PTI QuantaMaster model C-60SE spectrofluorimeter, equipped with a 928 PMT detector and corrected for detector response. The emission was found to be uniform throughout the area of each device.

Results and Discussion

Benzocyclobutene (BCB) was used as the cross-linking unit in the preparation of the hole-transporting copolymer. The thermal cross-linking of BCB (Scheme 1) occurs effectively between 180 °C and 250 °C through ring opening of the four-membered cyclobutene ring followed by irreversible cycloaddition to form a cyclooctadiene ring.[37] The advantages of the robust cyclooctadiene cross-linking unit include its stability to air, moisture, and light as well as its lack of reactivity post-cross-linking. In addition, the low reactivity of the BCB precursor below 150 °C allows a wide range of chemistry to be performed in its presence. The TPD−BCB copolymer (containing ∼9 mol % of BCB) was prepared using AIBN as the initiator as shown in Scheme 1 affording the desired copolymer in 86% yield as a white powder soluble in common organic solvents such as chloroform, THF, and chlorobenzene.

The thermal properties of the copolymer were investigated by differential scanning calorimetry (DSC). As shown in the inset of Figure 1, the TPD−BCB copolymer has a weak glass transition temperature (T_g) near 175 °C. Since the polymer is amorphous, the crystallization that affects small molecular TPD is no more an issue,[38] thus eliminating one of the major origins of the degradation in OLEDs. After having been isothermally heated at 250 °C for 60 min, the sample was cooled to room temperature and then rescanned. In the second heating, a broader glass transition centered near 190 °C was observed with no other thermal feature apparent above 200 °C. The difference observed between the first and the second scan in the DSC is believed to reflect the cross-linking of the copolymers after thermal treatment.

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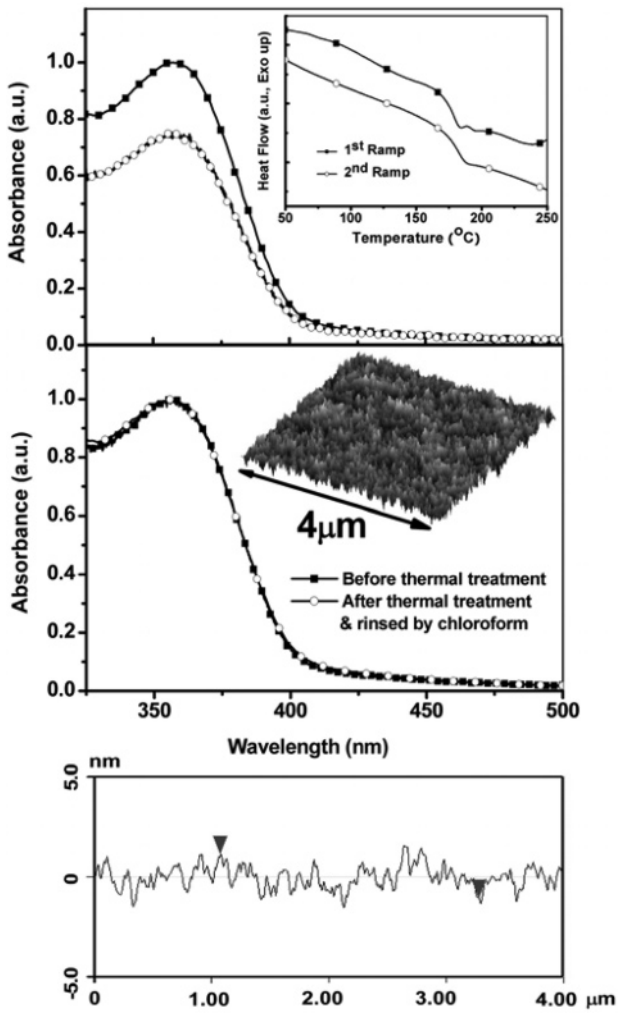


Figure 1. UV/vis absorbance of the TPD−BCB copolymer films before (■) and after thermal treatment (○): annealing at 170 °C for 2 h and cross-linking at 200 °C for (a) 2 h and (b) 4 h, followed by solvent rinsing. The inset at the top shows the DSC of the copolymer, and the inset in the middle shows AFM imaging of cross-linked film on silicon substrate with the cross section profile at the bottom.

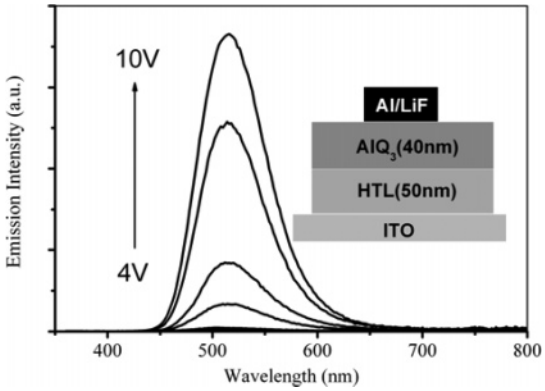


Figure 2. EL spectra of the device ITO/cross-linked TPD−BCB copolymer (50 nm)/AlQ3 (40 nm)/LiF (1 nm)/Al (1000 nm) at bias voltages from 4 V to 10 V. The inset shows the device structure of bilayer fluorescent OLED.

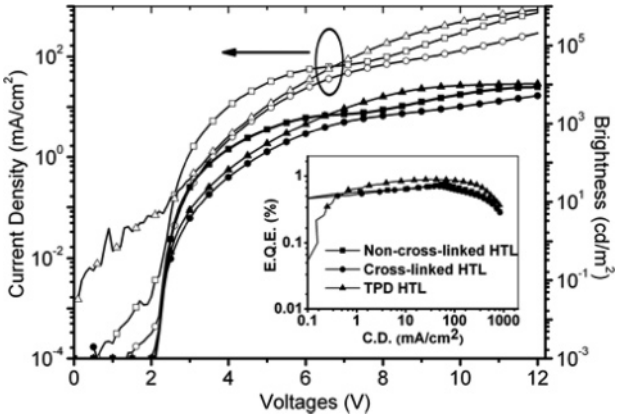


Figure 3. Current-voltage and brightness-voltage characteristics for AlQ_3 fluorescent devices with the non-cross-linked TPD−BCB copolymer (squares: ■, □), cross-linked TPD−BCB copolymer (circles: ●, ○), and small molecular TPD (triangles: ▲, Δ) as HTL. The inset shows the corresponding external quantum efficiencies vs current density for devices.

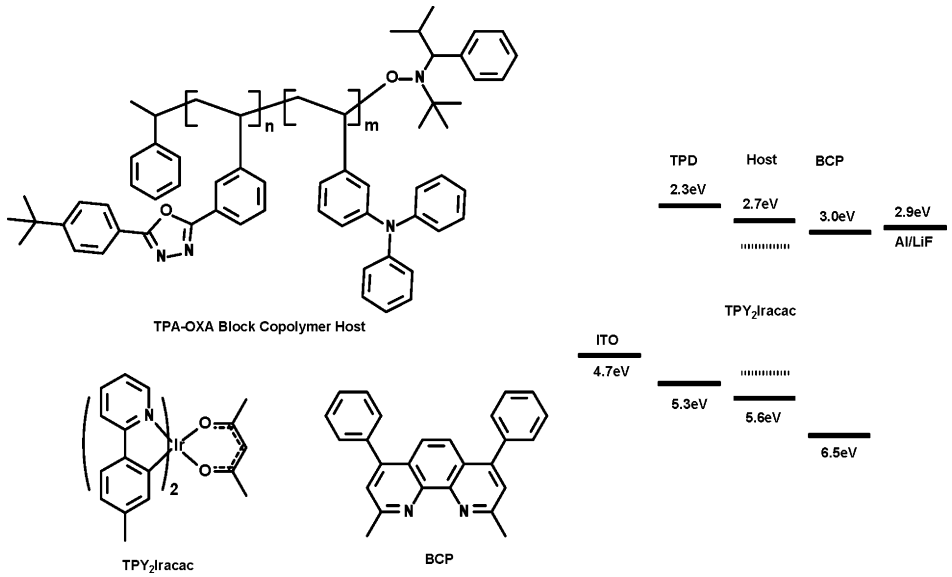
The properties of the cross-linkable copolymer were monitored using UV/vis spectroscopy, ellipsometry, and atomic force microscopy (AFM). Uniform films were formed on glass substrates by spin-coating of a solution of the TPD−BCB copolymer in chloroform. Thin film samples were then thermally treated under different conditions. The resistance of the thermally treated films to chloroform solvent was then investigated via UV/vis spectroscopy as shown in Figure 1. The results show the TPD−BCB copolymer is completely resistant to common organic solvents after thermal treatment, i.e., annealing at 170 °C for 2 h followed by cross-linking at 200 °C for 4 h in a glovebox. As the absorption spectrum of the polymer film is transparent over the entire visible region, this cross-linked layer can be used for the bottom layer of OLEDs without affecting the light output of the device. In addition to solvent resistance, surface topology of the polymer films after thermal cross-linking is critical to device performance. Thus, ellipsometry and AFM were used to investigate the surface properties of the films before and after cross-linking. A 13 mg/mL solution of this copolymer in chloroform was spin-coated on silicon wafers (2 cm × 2 cm) at 3000 rpm to produce films with an ellipsometric thickness of 62 nm. The films were then thermally treated as described above. Annealing at 170 °C for 2 h—near the glass transition but below the cross-linking temperature of the TPA-BCP copolymers—helped to form a smooth surface. After heating at 200 °C for 4 h to cross-link and anneal, rinsing the film with chloroform led to little change in thickness (<2 nm) over the entire surface of the film. The inset of Figure 1 shows an AFM image of the polymer film after thermal cross-linking. It was found that the thin film retained a mirrorlike smoothness with a root-mean-square (rms) surface roughness of 0.51 nm, which is much smaller than a typical value of >1.0 nm for the PEDOT:PSS film on the indium tin oxide (ITO) surface.[30]

The hole-transporting properties of our novel TPD−BCB copolymer were then evaluated in an OLED configuration. Therefore, bilayer fluorescent OLEDs were first fabricated with a device structure involving ITO/HTL (50 nm)/AlQ_3 (40 nm)/LiF (1 nm)/Al (100 nm) (Figure 2), in which ITO and LiF/Al act as anode and cathode, respectively, and the vapor deposited AlQ_3 works as both an electron-transporting layer and an emitting layer. This device structure was chosen because of its simple architecture that leads to easy interpretation of observed data. Such a device structure is both easy to fabricate and to compare with AlQ_3 data in the literature. For the purpose of comparison, the HT materials used in our study included the non-cross-linked TPD−BCB

Table 1. Summary of Devices Performance for Both Fluorescent and Phosphorescent OLEDs Fabricated

	AlQ_3 fluorescent devices			$TPY_2Iracac$ phosphorescent devices	
HTL	not cross-linked	cross-linked	TPD	cross-linked	N/A
turn-on voltages (0.1 cd/m^2)	2.5 V	2.5 V	2.5 V	5 V	6.4 V
max. EQE, brightness	0.76%, 1600 cdm^{-2}	0.7%, 1000 cdm^{-2}	0.89%, 1500 cdm^{-2}	10.4%, 350 cdm^{-2}	6.4%, 160 cdm^{-2}
max. brightness, voltage	8600 cdm^{-2}, 12 V	5200 cdm^{-2}, 12 V	10400 cdm^{-2}, 12 V	2540 cdm^{-2}, 27 V	6000 cdm^{-2}, 26.8 V
EQE at 800 cdm^{-2}	0.71%	0.7%	0.88%	9.1%	6.0%

Scheme 2. Chemical Structures of Materials Used in Fabrication of Phosphorescent OLEDs and the Energy Diagram for the Trilayer Phosphorescent Device



copolymer, the thermally cross-linked TPD−BCB copolymer, and the corresponding vapor deposited small molecule TPD. Measurements obtained using this set of devices enabled an evaluation of the influence on both the cyclobutene unit and the thermal cross-linking step on device performance.

All the devices show voltage independent pure emission from AlQ_3, which means that charge recombination occurs exclusively within the AlQ_3 layer. The electroluminescent spectra for the device using the cross-linked copolymer as HTL are shown in Figure 2, while current-voltage and brightness-voltage plots for the three devices are shown in Figure 3. We find that all three devices have very similar performances with turn on voltages of about 2.5 V (voltage at 0.1 cd/m^2) and light output exceeding 5000 cd/m^2 at 12 V. From the I−V curves, it is seen that the thin polymer films exhibit both good hole injection and transport properties comparable to those of a vapor deposited small molecule TPD layer. Cross-linking only leads to a small drop in conductivity of the polymer. As shown in the inset of Figure 3, there is little difference in the external quantum efficiencies (EQE) between these three devices. The EQE reaches 0.76% for the device with the non-cross-linked copolymer as a hole-transporting layer, 0.7% for the cross-linked copolymer, and 0.89% for the device with vapor deposited TPD. Such device performances, summarized in Table 1, are quite respectable for this very simple type of device configuration. All of the results suggest that the cross-linkable TPD−BCB copolymer can work very well as a hole-transporting material for OLEDs application. Therefore we tested the potential use of the cross-linked copolymer in more performing solution-processed multilayer phosphorescent devices.

A trilayer phosphorescent device was assembled with the structure shown in Figure 4. The cross-linked TPD−BCB copolymer (65 nm) HTL layer was prepared on ITO by annealing at 170 °C for 2 h followed by cross-linking and annealing at 200 °C for 4 h. Following this thermal treatment an 80 nm layer of polymer (TPA-OXA block copolymer host with $m/n = 1$)[39] doped with 8 wt % green emitting iridium complexes ($TPY_2Iracac$) was spin coated on top. The electron-transporting and hole-blocking layer of BCP (40 nm) was then vapor deposited in a high vacuum chamber followed by the metal cathode consisting of LiF (1 nm) and Al (100 nm). The chemical structures of the materials used as well as the device energy diagram are shown in Scheme 2. Another device without an HTL was constructed at the same time for comparison purposes. Figure 4 shows the electroluminescent spectrum for trilayer phosphorescent devices with the structure shown as inset. A pure green emission (peak at 523 nm) from the doped iridium complexes was observed, which indicates that recombination primarily occurs in the emitting layer, and there is efficient energy transfer from the host polymer to the green emitting dopants. No emission from the cross-linked hole-transporting layer was observed, which is also consistent with its high lowest occupied molecular orbital (LUMO) level (2.3 eV). In other words, this cross-linked layer not only acts as hole-transporting layer but also as electron blocking layer.

Figure 5 shows the current-voltage and brightness-voltage characteristics as well as external quantum efficiency vs current density for two electrophosphorescent devices, one

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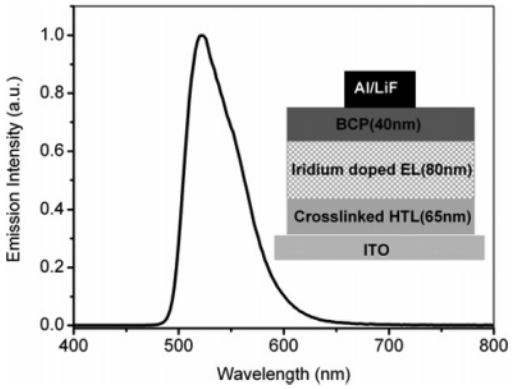

Figure 4. EL spectrum of phosphorescent device of the ITO/cross-linked TPD−BCB copolymer (65 nm)/TPY_2Iracac doped polymer EL (80 nm)/BCP (40 nm)/LiF (1 nm)/Al (100 nm). The inset shows the phosphorescent device structure using cross-linked HTL.

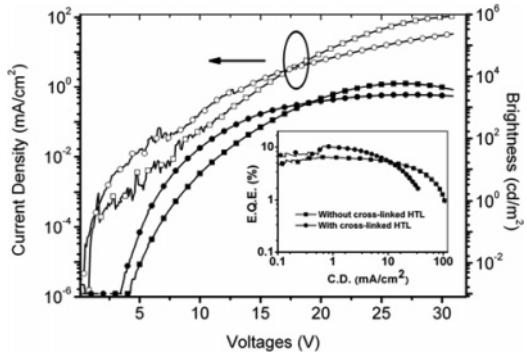

Figure 5. Current-voltage and brightness-voltage characteristics for phosphorescent devices with cross-linked TPD−BCB copolymer as HTL (circles: ●, ○) and without HTL (squares: ■, □). The inset shows the corresponding external quantum efficiencies vs current density for devices.

with a cross-linked HTL and the other without an HTL. Table 1 lists some important device results. High brightness reaching 2500 cd/cm^2 at 20 V and 6000 cd/cm^2 at 27 V was achieved for devices with and without cross-linked HTL, respectively. It is found that the turn-on voltage for the device with a cross-linked HTL is about 5.0 V, which is lower than the 6.4 V needed without an HTL. This is not surprising when the device energy diagram of Scheme 2 is considered: insertion of the HTL working as a step layer to assist with charge transport decreases the injection barrier between ITO and emitting layer. This is also evidenced by the finding that at low voltages, the current density of the device with HTL is higher than that without HTL. At high voltages, the charge transport is no longer determined by the injection barriers but the conductance of the organic layers, which is affected by their thickness. As a result, the thicker device with cross-linked HTL has a lower current density than that of the thinner device without HTL. In addition to lowering the turn-on voltage, the cross-linked HTL also dramatically increases the EQE when compared to the device without this layer. The EQE reaches 10.4% for the triple-layer device, while the highest efficiency achieved for a comparable device without this layer is only 6.4%. This increase is due to two major factors; first, the high LUMO level of the TPD polymer helps in confining exciton formation to the emitting layer; in addition, the recombination area is shifted toward the middle of the device thus avoiding the quenching of excitons by the anode. With the increase in current density, the quantum efficiencies of two devices roll off significantly, as observed for other electrophosphorescent devices.[4,6,9]

Conclusion

In conclusion, a novel thermally cross-linkable hole-transporting polymer has been successfully developed and applied for OLEDs. This copolymer could be completely cross-linked to form smooth insoluble films through reaction of the benzocyclobutene (BCB) units at 200 °C. Fluorescent devices with copolymers as HTL exhibit similar behavior before and after cross-linking. A comparison of the polymer to vacuum deposited small molecule TPD shows only a slight change in device performance, suggesting that replacement of the normally vacuum-deposited layer by our solution-processible polymeric system is feasible. Using this novel thermally cross-linkable polymer, a highly efficient solution-processed multilayer green emitting phosphorescent devices with EQE = 10.4% at 350 cd/m^2 was demonstrated. As all of our device testing to date was carried out in air, a study of reliability and lifetime remains to be done. We are continuing our study of cross-linkable emitting and electron injection layers in order to achieve the goal of a fully organic solution-based polymer device.

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