Article

Journal of
Nanoscience and Nanotechnology
Vol. 19, 4705–4709, 2019
www.aspbs.com/jnn

Thermally Cross-Linkable Styrene-Based Host Materials for Solution-Processed Organic Light-Emitting Diodes

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Thermally cross-linkable host materials, DV-TPACZ, DV-TPADBCZ, and TV-TPBI, were designed and synthesized for solution-processed organic light-emitting diodes (OLEDs). The synthesized styrene-functionalized host materials were thermally cross-linked by curing at 150–200 °C without using a polymerization initiator. Excellent solvent resistance was observed for all cured host films. They exhibited low highest occupied molecular orbital energy levels of 5.4–5.7 eV, which indicated a low hole injection barrier from the hole transport layer to the emissive layer. A solution-processed red phosphorescent OLED with 5 wt% $(MPHMQ)_2Ir$ (tmd) dopant in the thermally cross-linkable DV-TPACZ host exhibited a current efficiency of 5.3 cd/A, power efficiency of 3.2 lm/W, and external quantum efficiency of 3.6%.

Keywords: Thermally Cross-Linkable Host, Organic Light-Emitting Diode, Phosphorescence, Styrene, Solvent Resistance.

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) have been considered as the most competitive candidates for solid-state lighting and new-generation full-color flat-panel displays owing to advantages such as fast response, wide visual angle, low operating voltage for low power consumption, high brightness, high contrast, and the possibility to produce thin, large-area, and flexible devices.[1,2] Solution-processed OLEDs that are prepared by the incorporation of phosphorescent dopants in macromolecules or polymer hosts have generated a lot of interest in recent years because they can harvest both singlet and triplet excitons and also overcome the demerits of vacuum deposition processes.[3–7] However, multilayer OLED fabrication from solutions requires that each underlying layer be resistant to the solvent used for the deposition of the next layer. A simple approach to solve this problem involves the use of an orthogonal solvent for spin-casting to deposit the subsequent layers. Yet another approach involves using a cross-linkable material, which can be solution-processed by spin-casting and then transformed into an insoluble film by light or thermal treatment.[8,9] However, the light-induced cross-linking process may lead to quenching of excitons by the photochemical initiator.[10] In contrast, thermally cross-linkable materials are attractive because they do not degrade the performance of the light-emitting device. In particular, styrene-based materials have attracted a lot of attention as thermally cross-linkable host materials for OLEDs, because free radicals are generated from a Diels-Alder styrene dimer by curing at 150–200 °C.[11–14]

In this study, we designed and synthesized styrene-functionalized thermally cross-linkable host materials, DV-TPACZ, DV-TPADBCZ, and TV-TPBI, based on 4-(9*H*-carbazolyl)triphenylamine (TPACZ), 4-(3,6-di-*tert*-butyl-9*H*-carbazolyl)triphenylamine (TPADBCZ), and 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1*H*-benzimidazole) (TPBI). The synthesized host materials with styrene groups were thermally cross-linked by curing at 150–200 °C without any polymerization initiator. Excellent solvent resistance was observed for all cured host material films. In particular, a solution-processed red phosphorescence device using DV-TPACZ as a thermally cross-linkable host was fabricated and its performance was evaluated. The detailed synthetic routes and chemical structures of the thermally cross-linkable host materials are outlined in Scheme 1.

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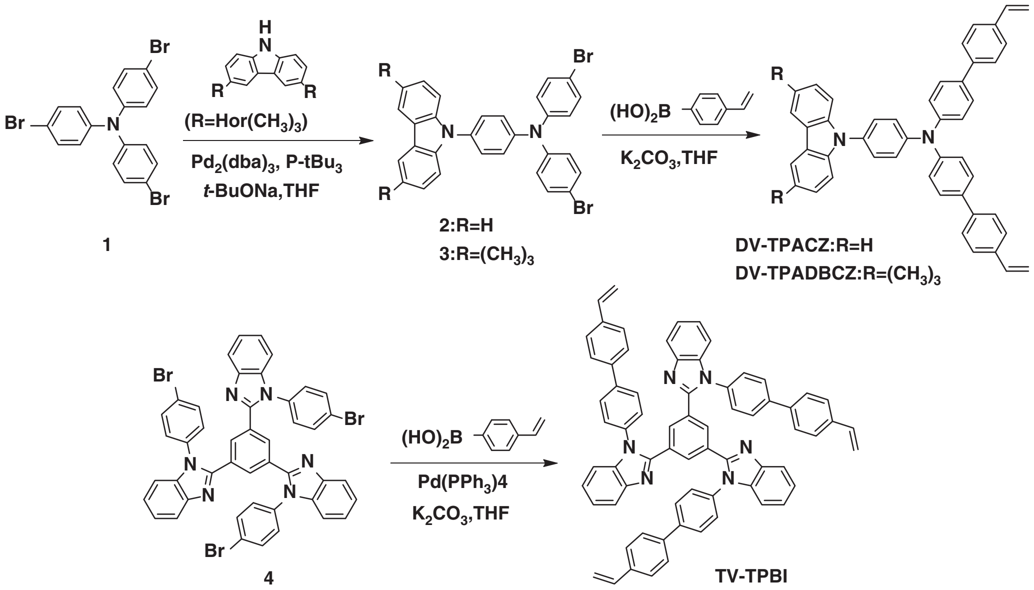

Scheme 1. Synthesis of DV-TPACZ, DV-TPADBCZ, and TV-TPBI.

2. EXPERIMENTAL DETAILS

2.1. Materials

All chemicals were purchased from Sigma-Aldrich and Alfa Aesar and used without further purification. Compounds **2** and **4** were synthesized according to the methods described in previous reports.[15, 16] All spectra matched with previously reported data.

2.2. Synthesis of Thermally Cross-Linkable Host Materials

2.2.1. Synthesis of 4-Bromo-N-(4-bromophenyl)-N-(4-(3,6-di-tert-butyl-9H-carbazol-9-yl) phenyl)Aniline(3)

Compound **1** (5.0 g, 10.4 mmol), 3,6-di-*tert*-butylcarbazoleoride (1.53 g, 5.46 mmol), sodium *tert*-butoxide (2.10 g, 21.8 mmol), tri-*tert*-butylphosphine (0.66 mL of 1 M solution, 0.66 mmol), and $Pd_2(dba)_3$ (0.3 g, 0.33 mmol) were dissolved in toluene and refluxed with stirring for 24 h under a nitrogen atmosphere. Subsequently, the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure to give a crude residue. The crude product was purified by silica gel column chromatography (ethyl acetate/hexane, 1/4, *v/v*) and compound **3** was obtained as a pale green solid (1.71 g, 43%). ^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm): 8.18 (*s*, 2H), 7.41 (*m*, 12H), 7.20 (*d*, 2H, $J = 7.5$ Hz), 7.02 (d, 2H, $J = 7.5$ Hz), 1.47 (*s*, 18H); MALDI-TOF (M^+, $C_{38}H_{36}Br_2N_2$): Calcd. 677.23, found 678.12.

2.2.2. Synthesis of Host Materials

Compound **2** (1.5 g, 2.64 mmol), 4-vinylphenylboronic (0.47 g, 3.17 mmol), and $Pd(PPh_3)_4$ (0.09 g, 0.08 mmol) were dissolved in tetrahydrofuran. A solution of 2 M K_2CO_3 and Aliquat 336 (0.10 g, 0.26 mmol) was added to the reaction flask and the mixture was refluxed for 24 h with stirring under a nitrogen atmosphere. Subsequently, the reaction mixture was cooled to room temperature and extracted with ethyl acetate. The combined organic extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure to obtain a crude residue. The crude product was then purified by silica gel column chromatography (ethyl acetate/hexane, 1/2, *v/v*) to obtain DV-TPACZ as a pale green solid (0.8 g, 51%). DV-TPADBCZ and TV-TPBI were prepared using compounds **3** and **4**, respectively, following the same procedure.

DV-TPACZ (Yield = 51%): ^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm): 8.15 (*d*, 2H, $J = 9.0$ Hz), 7.57 (*m*, 8H), 7.46 (*m*, 10H), 7.29 (*m*, 8H), 6.77 (*dd*, 2H, $J = 11$, 18 Hz), 5.80 (*d*, 2H, $J = 18$ Hz), 5.27 (*d*, 2H, $J = 11$ Hz); MALDI-TOF (M^+, $C_{46}H_{34}N_2$): Calcd. 613.88, found 614.27.

DV-TPADBCZ (Yield = 35%): ^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm): 8.19 (*s*, 2H), 7.60 (*m*, 8H), 7.46 (*m*, 10H), 7.27 (*m*, 6H), 6.78 (*dd*, 2H, $J = 16.9$, 11.4 Hz), 5.79 (*d*, 2H, $J = 16.9$ Hz), 5.22 (*d*, 2H, $J = 11.4$ Hz), 1.46 (*s*, 18H); MALDI-TOF (M^+, $C_{54}H_{50}N_2$): Calcd. 725.51, found 726.40.

TV-TPBI (43%): ^{1}H NMR (300 MHz, $CDCl_3$)δ (ppm): 7.90 (*s*, 3H), 7.80 (*d*, 3H, $J = 7.5$ Hz), 7.54 (*d*, 6H, $J = 8.1$ Hz), 7.43 (*m*, 12H), 7.26 (*m*, 9H), 7.13 (*d*, 6H, $J = 8.1$ Hz), 6.75 (*dd*, 3H, $J = 11.4$, 17.7 Hz), 5.80 (*d*, 3H, $J = 17.7$ Hz), 5.30 (*d*, 3H, $J = 11.4$ Hz); MALDI-TOF (M^+, $C_{69}H_{48}N_6$): Calcd. 959.89, found 960.39.

2.3. Measurements and Device Fabrication

Measurements and device fabrication were performed following methods described in previous reports.[11,13–16]

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization

Thermally cross-linkable host materials, DV-TPACZ, DV-TPADBCZ, and TV-TPBI were synthesized as shown in Scheme 1. The halogenated compounds, **2**, **3**, and **4**, were prepared following literature procedures.[15,16] Three host materials, DV-TPACZ, DV-TPADBCZ, and TV-TPBI were synthesized by a palladium-catalyzed Suzuki cross coupling reaction between **2**, **3**, or **4** and (4-ethenylphenyl)boronic acid and characterized by ^{1}H-NMR, ^{13}C-NMR, and MALDI-TOF mass spectrometry.

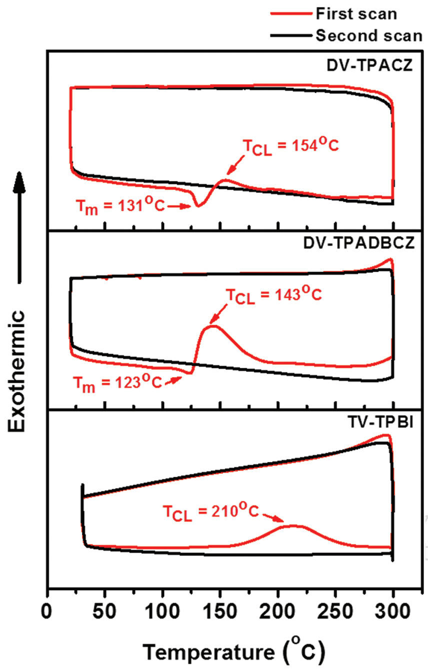

Figure 1. DSC curves of DV-TPACZ, DV-TPADBCZ, and TV-TPBI.

3.2. Photophysical Properties

Absorption and emission spectra of the synthesized host materials were measured in 10^{-5} M CH_2Cl_2 solutions. DV-TPACZ and DV-TPADBCZ exhibited similar absorptions at ∼290 and 350 nm, which were attributed to the n–π^* transitions of the carbazole moieties and the π–π^* charge transitions from carbazole to triphenylamine, respectively.[17–19] TV-TPBI showed a strong absorption at ∼290 nm that was attributed to the benzimidazole moiety. DV-TPACZ, DV-TPADBCZ, and TV-TPBI exhibited photoluminescence (PL) emissions at 447 nm, 453 nm, and 388 nm, respectively. The optical band gap energies of the host materials were 3.20, 3.10, and 3.70 eV for DV-TPACZ, DV-TPADBCZ, and TV-TPBI, respectively, as determined by the absorption edges. TV-TPBI showed the largest energy band gap among the three synthesized host materials. The triplet energy levels of DV-TPACZ, DV-TPADBCZ, and TV-TPBI were measured to be 2.70, 2.50, and 2.58 eV, respectively.

3.3. Electrochemical Properties

The electrochemical properties of the synthesized host materials were investigated by cyclic voltammetry (CV). The measurements were conducted using their dichloromethane solutions with tetrabutylammonium perchlorate as the electrolyte. The highest occupied molecular

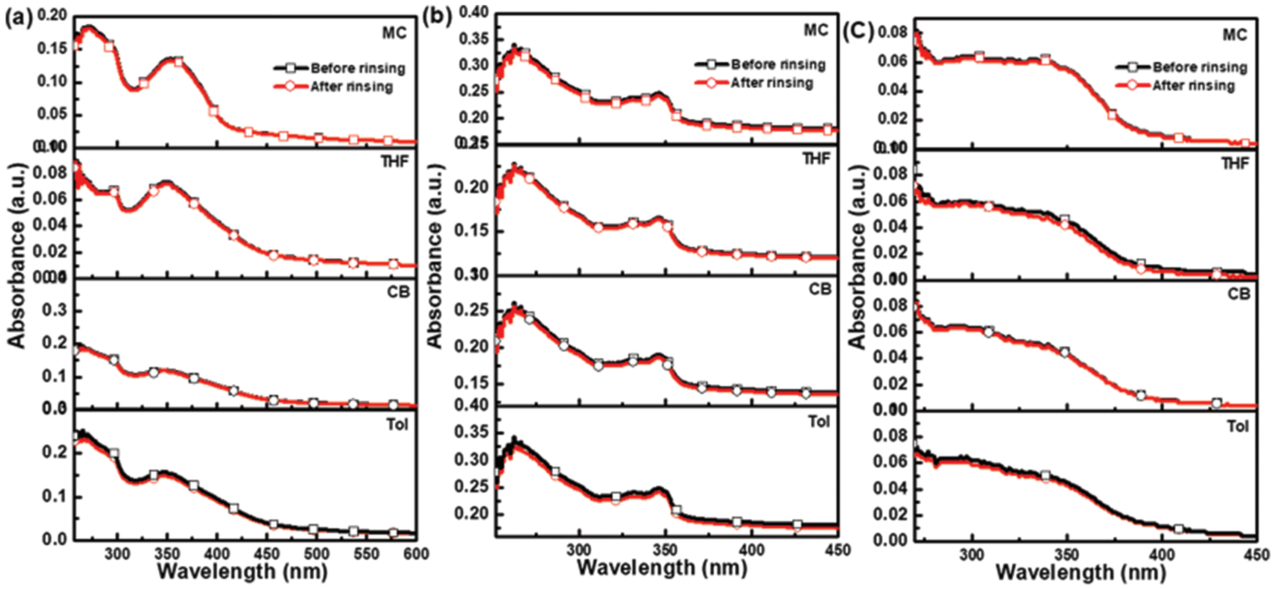

Figure 2. UV-vis absorption spectra of cured (a) DV-TPACZ, (b) DV-TPADBCZ, and (c) TV-TPBI films before and after rinsing with organic solvents (methylene chloride (MC), tetrahydrofuran (THF), chlorobenzene (CB), and toluene (Tol)).

orbital (HOMO) energy levels of DV-TPACZ, DV-TPADBCZ, and TV-TPBI were estimated to be −5.60, −5.40, and −5.70 eV versus Fc/Fc$^+$, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels of DV-TPACZ, DV-TPADBCZ, and TV-TPBI were calculated from the differences between the optical band gaps and the HOMO energy levels ($\Delta E_{\text{band gap}} = E_{\text{LUMO}} - E_{\text{HOMO}}$) to be −2.40, −2.30, and −2.0 eV, respectively. The HOMO and LUMO energy levels of the synthesized host materials were well matched with those of the previously reported $(\text{MPHMQ})_2\text{Ir(tmd)}$ (HOMO: −5.10 eV, LUMO: −3.10 eV) red dopant.[20]

3.4. Thermal Properties and Solvent Resistances

The thermal properties of the host materials were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The 5 wt% loss temperatures (T_d) of DV-TPACZ, DV-TPADBCZ, and TV-TPBI were 469, 428, and 486 °C, respectively. This result indicated that the synthesized compounds were sufficiently thermally stable to be applied in OLEDs as host materials. Figure 1 shows the first- and second-heating DSC curves of DV-TPACZ, DV-TPADBCZ, and TV-TPBI. These curves exhibited exothermic peaks in the range of 143–210 °C, which correspond to the thermal polymerization of the styrene group.[11–14] The curing temperatures (T_{CL}) of DV-TPACZ, DV-TPADBCZ, and TV-TPBI were 154, 143, and 210 °C, respectively. DV-TPACZ and DV-TPADBCZ showed endothermic peaks at 131 and 123 °C, respectively, which were followed by the exothermic peaks, indicating that styrene polymerization occurred in the partial melting state. In the second heating scan, no peaks were observed in the temperature range of 140–200 °C, which likely corresponded to the cross-linking of the styrene-functionalized host materials after thermal treatment. There has been no consensus on the correct thermal cross-linking mechanism of the styryl unit even though several mechanisms were proposed in previous reports. Two well-known mechanisms on the cross-linking reaction have been suggested by Mayo and Flory.[13] The solvent resistances of the cross-linked films were monitored using UV-Vis absorption spectroscopy. The thin films were obtained by spin-coating from dichloromethane solutions followed by thermal curing at 150 °C for 30 min under N_2 atmosphere. The results in Figure 2 show that the DV-TPACZ, DV-TPADBCZ, and TV-TPBI films exhibit unchanged UV-Vis absorbances after thermal curing followed by washing with common solvents such as methylene chloride, tetrahydrofuran, chlorobenzene, and toluene. These results confirmed that these host materials possessed suitable solvent resistance for multilayer integration by the solution process in OLEDs.

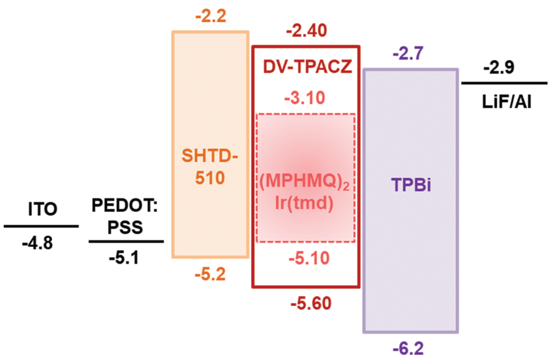

Figure 3. The energy level diagram of the fabricated device.

3.5. Electrophosphorescent OLEDs

Among the three synthesized host materials, DV-TPACZ was selected as the thermally cross-linkable host in red phosphorescent OLED with a device configuration of ITO (50 nm)/PEDOT:PSS (40 nm)/SHTD-510 (17 nm)/DV-TPACZ:$(\text{MPHMQ})_2\text{Ir(tmd)}$ (95:5%) (30 nm)/TPBI (40 nm)/LiF (1 nm)/Al (100 nm). The optimized device performance was obtained at 5 wt% concentration of the $(\text{MPHMQ})_2\text{Ir(tmd)}$ dopant. The device containing $(\text{MPHMQ})_2\text{Ir(tmd)}$ dopant with thermally cross-linked DV-TPACZ host showed the EL

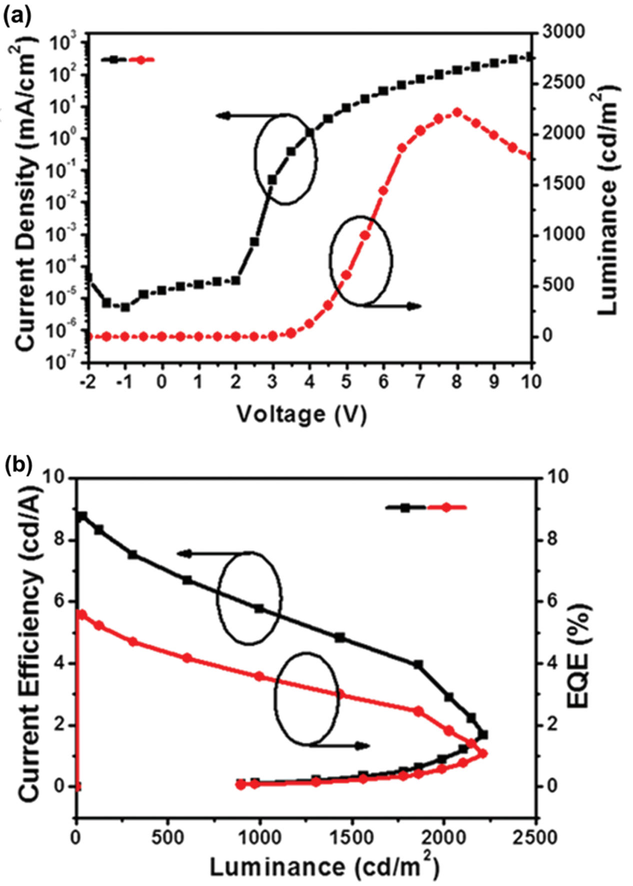

Figure 4. (a) Current density–voltage–luminance (*J–V–L*) and (b) external quantum efficiency-current density-current efficiency (EQE-J-CE) curves of the DV-TPACZ-based device.

maximum peak at 606 nm with CIE coordinates of (0.62, 0.36) unaffected by the applied voltage with a full-width at half-maximum (FWHM) values of 65 nm. The turn-on voltage ($V_{\text{turn-on}}$, defined as the bias at a luminance of 1 cd/m^2) of the device was 5.5 V, current efficiency of 5.3 cd/A, power efficiency of 3.2 lm/W, and external quantum efficiency of 3.6%. The device performances suggest that the energy levels of the employed materials are well matched (Fig. 3), leading to facile injection of holes and electrons, their transport across layers, and recombination. DV-TPACZ also showed hole-transporting property after film curing despite its low device performance. The I-V-L characteristics and the current efficiency–Luminance–EQE characteristics of the red phosphorescent OLEDs are shown in Figure 4.

4. CONCLUSION

Herein, we have described the synthesis of novel thermally cross-linkable styrene-functionalized host materials, DV-TPACZ, DV-TPADBCZ, and TV-TPBI, which were applied in solution-processed red phosphorescent OLEDs. These host materials showed thermal stability and excellent solvent resistance. The solution-processed OLED device based on the red phosphorescent $(MPHMQ)_2Ir(tmd)$ dopant in the thermally cross-linked DV-TPACZ host exhibited a current efficiency of 5.8 cd/A, power efficiency of 3.2 lm/W, and external quantum efficiency of 3.6% at 1,000 cd/m^2. After film curing, DV-TPACZ demonstrated hole-transporting property, which indicated that it could be applied as a thermally cross-linkable host material in solution-processed OLED.

Acknowledgment: This research was supported by the Ministry of Trade, Industry and Energy (MOTIE, Korea) under the Industrial Technology Innovation Program. No. 10067715, and with the assistance of National Research Foundation (NRF) grants funded by the Korean government (Grant Nos. NRF2017R1A2A2A05001345 and 2011-0030013 through GCRC SOP).

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Received: 29 May 2018. Accepted: 10 September 2018.