Novel 9,9'-(1,3-Phenylene)bis-9H-carbazole-Containing Copolymers as Hole-Transporting and Host Materials for Blue Phosphorescent Polymer Light-Emitting Diodes

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ABSTRACT: Novel photo-crosslinkable hole-transport and host materials incorporated into multilayer blue phosphorescent polymer light-emitting diodes (Ph-PLEDs) were demonstrated in this study. The oxetane-containing copolymers, which function as hole-transport layers (HTL), could be cured by UV irradiation in the presence of a cationic photoinitiator. The composition of the two monomers was varied to yield three different hole-transporting copolymers, [Poly(9,9'-(5-(((4-(7-(4-(((3-methyloxetan-3-yl)methoxy)methyl)phenyl)octan-3-yl)benz yl)oxy)methyl)-1,3-phenylene)bis(9H-carbazole)) (P(mCP-Ox)-I, -II, and -III)]. In addition, monomer 1 was copolymerized with styrene to produce copolymer P(mCP-Ph) as a host material for bis[2-(4,6-difluorophenyl)pyridinato-C²,N](picolinato)iridium(III) (Flrpic), a blue-emitting dopant. All mCP-based copolymers displayed high glass transition temperatures (T_q) of up to 130-140 °C and triplet energies of up to 3.00 eV. The blue Ph-PLEDs exhibited a maximum external quantum efficiency of 2.55%, in addition to a luminous efficiency of 8.75 cd A⁻¹ when using the device configuration of indium tin oxide/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)/**P(mCP-OX)-III/P(mCP-Ph)**:Flrpic(15 wt %)/3,3'-[5'-[3-(3-pyridinyl)phenyl] [1,1':3',1''-terphenyl]-3,3''-diyl]bispyridine/LiF/AI. The device bearing **P(mCP-Ox)-III** HTL, containing the highest composition of mCP unit, exhibited better performance than the other devices, which is attributed to induction of more balanced charge carriers and carrier recombination in the emissive layer. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 707–718

KEYWORDS: blue; copolymerization; crosslinking; curing of polymers; light-emitting diodes; luminescence; oxetane; phosphorescence; photo-crosslinking; polymer light-emitting diode; solution process; synthesis

INTRODUCTION Organic light-emitting diodes (OLEDs) have emerged as a fascinating technology for the development of advanced flat panel display and flexible displays and flexible display devices. The maturation of this technology for practical applications has been made possible by the development of a number of small organic molecules for use in fabricating the corresponding display devices. Most conventional OLED materials show semiconducting properties; fluorescent molecules, in particular, have been utilized for elaborating conventional RGB pixels. As an alternative to fluorescent molecules, phosphorescent dye molecules are particularly promising because both singlet and triplet excitons can generate unique light emissions with a theoretical internal quantum efficiency of 100%.¹⁻³ In particular, cyclometalated Ir(III) complexes show high phosphorescent efficiencies and are one of the most important classes of phosphorescent dyes under investigation at present.⁴⁻⁹

When preparing phosphorescent OLEDs (Ph-OLEDs), multilayered device configurations are usually designed employing various auxiliary carrier-transport and blocking layers to improve device efficiency. These devices are mainly fabricated by vacuum processes using a combination of various auxiliary and emitting layers. Besides practical vacuum deposition-based fabrication methods, an alternative solution processing technique for OLEDs involves solution spin coating. Advantages of the

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spin-coating technique over vacuum process include a significant reduction in production costs and the ability to coat larger areas; however, in solution-based preparation of multilayer OLEDs, the coated layers tend to be at least partially dissolved by the solvent used to apply subsequent layers. A common method used to overcome this obstacle is to render the applied polymer layer by crosslinking before the subsequent coating step. The crosslinking process for obtaining phosphorescent polymer light-emitting diodes (Ph-PLED) can be carried out *via* a variety of strategies such as thermal,^{10–12} light,^{13–22} or chemical treatment.^{23–25} Polymeric hole-transport materials and host materials can be designed and synthesized in this manner to facilitate efficient singlet and triplet energy transfer in the solid state.

On the other hand, the development of high-efficiency blue Ph-PLEDs still remains a challenge when compared to redand green-emitting materials because of the larger energy bandgap and higher triplet energy $(E_{\rm T})$ required for carriertransport polymeric materials and blue host polymers. In addition to high- $E_{\rm T}$ and high carrier mobility with balanced hole and electron transport, the practical use of blue host polymers also necessitates the improvement of thermal and morphological stabilities in order to boost efficiencies. Various types of high- $E_{\rm T}$ small molecules have been synthesized as a component of hole-transport and host polymers for blue Ph-PLEDs. Among the common large bandgap materials, carbazole is the most widely used hole-transport moiety because of its high $E_{\rm T}$ and rigid molecular framework. The derivative 1,3-bis(N-carbazolyl)benzene (mCP) is also a wellknown high- $E_{\rm T}$ molecule, which can be utilized as a polymer side chain. In addition to suitable electronic properties and charge balance for blue Ph-PLEDs, the thermal properties of host polymers remain a key consideration in their design, since long-term device stability is thought to be dependent on glass transition temperatures (T_g) of the host materials.

In blue Ph-PLEDs, large bandgap host materials such as mCP-containing polymers with a triplet energy higher than that of the phosphorescent Ir(III) complex should be employed to avoid back-energy transfer from the Ir(III) complex to the host polymer. Because of the high highest occupied molecular orbital (HOMO) energy level of these large-bandgap polymers, the efficiency of the hole injection from an indium tin oxide (ITO) electrode to the emissive layer (EML) can be suppressed if only a single hole-injection layer (HIL) is used in the device. Therefore, an additional hole-transport layer (HTL) or HIL can be combined with a conventional HIL material to form an optimal cascade energy profile to achieve efficient hole injection and charge confinement. For the fabrication of multilayered devices solely by solution processing, either photo- or thermally crosslinked hole-transporting materials are frequently used.^{10–22}

Here, we demonstrate the fabrication of photo-crosslinkable copolymers bearing mCP groups (monomer 1) and oxetane moieties (monomer 2) functioning as hole-transport units in the side chain, denoted by P(mCP-Ox). An oxetane group

was selected as the side chain of the copolymer to obtain a polymeric HTL because an oxetane group can undergo fast cationic polymerization in bulk with high conversion and low volume shrinkage, thus avoiding cracks in the spin-coated layers.^{26,27}

Three kinds of P(mCP-Ox) copolymers were successfully synthesized and applied as HTL coatings on a poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) ionomeric layer, followed by photo-crosslinking phenomenon under UV light irradiation. In order to fabricate an emitting layer, a solution of high- E_T **P(mCP-Ph)** as the blue host material mixed with bis[2-(4,6 difluorophenyl)pyridinato-C²,N](picolinato) iridium(III) (FIrpic) was spin-coated on top of the photo-crosslinked HTL polymer layer without any observable detrimental effects on the underneath layer. The functionality of each oxetane-containing polymeric HTL was investigated in terms of the device efficiency for solutionprocessed Ph-PLEDs. Solution-processed blue Ph-PLEDs using photo-crosslinked HTL (P(mCP-Ox)-III) containing larger proportion hole-transport mCP units (i.e., monomer 1) showed improved device performance compared to those containing crosslinked P(mCP-Ox)-I and -II-based HTLs. The corresponding PLED fabricated with P(mCP-Ox)-III and 15 wt % of FIrpic-doped P(mCP-Ph) showed the highest external quantum efficiency of 2.55% and luminous efficiency of 8.75 cd A^{-1} in addition to its low roll-off behavior.

EXPERIMENTAL

General Considerations

Commercial reagents were purchased from Sigma-Aldrich, TCI, or Acros Organics, and used without any purification unless stated otherwise. The radical initiator, α, α' -azobisisobutyronitrile (AIBN) was recrystallized in acetone before use. HPLC-grade toluene was purchased from Samkyung Chemical and distilled from CaH₂ before use. All reactions were performed under an argon atmosphere unless otherwise stated.

Synthetic Procedures

Compounds **2**, **3**, and **9** were synthesized by following the modified literature method. $^{28-30}$

Tert-butyl((3,5-dibromobenzyl)oxy)dimethyl silane (4)

Compound **3** (5 g, 18 mmol) and imidazole (1.92 g, 28 mmol) were dissolved in 200 mL dichloromethane (CH_2Cl_2) under argon. *Tert*-butyldimethylsilyl chloride (TBDMS-Cl, 4.25 g, 28 mmol) was added into the mixture and the mixture was allowed to stir at room temperature for 3 h. After reaction completion, the reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was then dried over Na_2SO_4 and concentrated under reduced under pressure. The resulting dark brown oil was purified by silica gel column chromatography with hexane as an eluent to give **4** in 98% yield (7.00 g).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.52 (s, 1H), 7.37 (s, 2H), 4.65 (s, 2H), 0.92 (s, 9H) 0.09 (s, 6H); ¹³C NMR (100

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MHz, CDCl₃): δ (ppm) 143.82, 136.74, 132.64, 132.48, 124.56, 123.98, 67.32, 25.74, 25.68, 25.66.

9,9'-(5-(((Tert-butyldimethylsilyl)oxy)methyl)-1,3phenylene)bis(9H-carbazole) (5)

Compound 4 (5 g, 13 mmol) and carbazole (4.83 g, 28 mmol) were dissolved in 30 mL toluene under argon. Sodium tert-butoxide (NaOt-Bu; 6.32 g, 65 mmol) was added to the mixture, which was then stirred at 60 $^\circ\text{C}$ for 1 h. Next, tris(dibenzylidene acetone)dipalladium(0) (Pd₂(dba)₃; 0.60 g, 0.65 mmol) and tri-tert-butylphosphine $(P(t-Bu)_3, 0.13 \text{ g}, 0.65 \text{ mmol})$ were added into the mixture, which was then heated to 110 °C. After stirring for 8 h, the reaction mixture was extracted with CH₂Cl₂ and washed with water. The organic layer was then dried over Na₂SO₄ and concentrated under reduced pressure. The resulting dark brown oil was purified by silica-gel column chromatography (CH₂Cl₂: hexane = 1:3 v/v) to give **5** in 70% yield (5.08 g).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.28 (d, J = 7.68 Hz, 4H), 7.75 (s, 1H), 7.73 (s, 2H), 7.60 (d, J = 8.22 Hz, 4H), 7.46 (t, 4H), 7.31(t, 4H), 5.02 (s, 2H), 0.90 (s, 9H), 0.13 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 142.68, 142.43, 139.72, 139.68, 139.60, 126.65, 122.69, 121.33, 119.74, 110.67, 109.45, 30.59.

(3,5-Di(9H-carbazol-9-yl)phenyl) methanol (6)

Compound **5** (5.0 g, 9.04 mmol) was dissolved in THF under argon. A 3-M solution of HCl (27 mL) was added dropwise into the mixture. The reaction mixture was allowed to stir at room temperature for 4 h. After reaction completion, the mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was then dried over Na_2SO_4 and concentrated under reduced pressure. The product was obtained by precipitation into hexane to provide **6** in 93% yield (3.68 g).

¹H NMR (300 MHz, CDCl₃) : δ (ppm) 8.19 (d, J = 6.00 Hz, 4H), 7.77 (s, 1H), 7.74 (s, 2H), 7.58 (d, J = 6.00 Hz, 4H), 7.47 (t, 4H), 7.34 (t, 4H), 4.98 (d, J = 6.00 Hz, 2H), 2.03 (t, 1H), ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 145.01, 140.79, 139.75, 126.51, 126.47, 126.41, 126.40, 126.37, 126.32, 124.46, 124.31, 124.12, 123.97, 123.85, 120.75, 120.66, 120.60, 120.55, 120.54, 110.02, 109.95, 109.86, 104.99, 77.58, 77.26, 76.94, 64.87, 64.68, 64.49.

9,9'-(5-(((4-Vinylbenzyl)oxy)methyl)-1,3-phenylene)bis(9H-carbazole) (7)

NaH (0.12 g, 5.01 mmol) was suspended in 35-mL anhydrous DMF at 0 °C. Compound 5 (2.0 g, 4.56 mmol) in DMF was added dropwise into the mixture and the mixture was allowed to stir for 1 h. Next, 1-(chloromethyl)-4-vinylbenzene (0.76 g, 5.01 mmol) in DMF was also added dropwise at 0 °C over a 15-min period; the reaction mixture was then stirred at room temperature for 12 h. After the reaction was completed, the reaction mixture was extracted with CH_2Cl_2 and washed with water; the mixture was extracted again with diethyl ether and washed with water. The combined organic layers were dried over Na₂SO₄ and concentrated

under reduced pressure. The oily product was purified by silica gel column chromatography (CH_2Cl_2 :hexane = 1:2 v/v) to give 7 in 72% yield (1.82 g).

¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.19 (d, J = 7.58 Hz, 4H) 7.77 (s, 1H), 7.74 (s, 2H), 7.58 (d, J = 8.22 Hz, 4H), 7.47 (t, 4H), 7.41 (d, J = 4.68 Hz, 4H), 7.34 (t, 4H), 6.74 (q, 1H), 5.80 (d, J = 17.58 Hz, 1H), 5.29 (d, J = 10.58 Hz, 1H), 4.78 (s, 2H), 4.72 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) : δ (ppm) 142.43, 142.38, 139.75, 139.72, 139.68, 138.4, 136.44, 128.7, 126.59, 122.54, 122.46, 122.02, 121.58, 121.50, 109.48, 109.43, 109.39, 72.54.

General Procedure for Polymerization

Poly(9,9'-(5-(((4-(7-(4-(((3-methyloxetan-3yl)methoxy)methyl)phenyl)octan-3-yl)benzyl)oxy)methyl)-1,3-phenylene)bis(9H-carbazole)) (P(mCP-Ox))

A solution of monomer **1** (**7**) and monomer **2** (**9**) (at a feeding molar ratio of 7:9 = m:n) in anhydrous toluene was degassed under nitrogen for 30 min. AIBN (0.41 mg, 0.0025 mmol) was added to the mixture and heated to 80 °C. The reaction mixture was allowed to stir at 80 °C for 48–60 h. The resultant polymer was then precipitated in methanol. The crude polymer was collected by filtration and then purified by Soxhlet extraction with acetone and chloroform, successively. The final product was obtained by precipitation of the chloroform solution into methanol. The pure copolymer was dried under vacuum for 24 h.

P(*mCP-Ox*)-*I*. Molar feeding ratio (*m*:*n* = 1:1); yield: 47.62%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.90 (br, 2H), 7.34 (br, 8H), 6.80 (br, 2H), 6.27 (br, 2H), 4.22 (br, 4H), 3.22 (br, 1H), 1.11 (br, 3H); anal. calcd.: C 83.9; H 6.85; N 3.48.

P(mCP-Ox)-II. Molar feeding ratio (*m*:*n* = 1:2); yield: 61.97%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.90 (br, 3H), 7.34 (br, 11H), 6.80 (br, 2H), 6.27 (br, 2H), 4.22 (br, 5H), 3.22 (br, 1H), 1.11 (br, 4H); anal. calcd.: C 83.66; H 6.39; N 3.57.

P(*mCP*-*Ox*)-*III.* Molar feeding ratio (*m*:*n* = 1:4); yield: 46.30%; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.90 (br, 6H), 7.34 (br, 18H), 6.80 (br, 2H), 6.27 (br, 3H), 4.22 (br, 5H), 3.22 (br, 1H), 1.11 (br, 6H); anal. calcd.: C 82.80; H 6.08; N 4.24.

Poly(9,9'-(5-(((4-(7-phenyloctan-3-yl)benzyl) oxy)methyl)-1,3-phenylene)bis(9H-carbazole)) (P(mCP-Ph))

Monomer **1** (0.7 g, 1.26 mmol) and styrene (0.01 g, 0.14 mol) were dissolved in anhydrous toluene and degassed under nitrogen for 30 min. AIBN (0.41 mg, 0.0025 mmol) was added to the mixture, which was then heated to 80 °C for 120 h under argon. The mixture was poured into methanol to collect the precipitate. The crude polymer was collected by filtration and then purified by Soxhlet extraction with acetone and chloroform, successively. The final product was obtained by precipitation of chloroform solution into methanol. Then, the product was dried under vacuum for 24 h to obtain P(mCP-Ph) as a white solid in a yield of 60%.



¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.83 (br, 4H), 7.30 (br, 8H), 7.10 (br, 12H), 4.15 (br, 4H), 1.09 (br, 6H); anal. calcd.: C 86.66; H 5.58; N 5.19.

Instruments

¹H NMR spectra were recorded on a Varian Mercury NMR 300 and 400 MHz spectrometer (Varian, Palo Alto, CA) using deuterated chloroform (CDCl₃) purchased from Cambridge Isotope Laboratories (Andover, MA). Elemental analyses were performed using an EA1112 (Thermo Electron, West Chester, PA) elemental analyzer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using polystyrene as the standard and THF as an eluent at the Korean Polymer Testing and Research Institute, Seoul, Korea. (Waters GPC, Waters 515 pump, Waters 410 RI, $2 \times$ PLgel Mixed-B).

The thermal properties were studied under a nitrogen atmosphere on a Mettler differential scanning calorimetry (DSC) 821^e instrument (Mettler, Greifensee, Switzerland). Thermogravimetric analysis (TGA) was conducted on a Mettler TGA50 (temperature rate 10 °C min⁻¹ under nitrogen).

Absorption spectra of polymers were obtained using a UVvis absorption spectrometer (HP 8453, PDA type) in the wavelength range of 190–1100 nm. In order to prepare the film sample, the polymers were dissolved in chloroform, and the solution was spin-coated onto quartz glass and dried under vacuum thoroughly.

Photoluminescence (PL) spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer at room temperature and a Thermo FA-357 fluorescence spectrophotometer at 77 K. The triplet energy of the polymers was determined by the highest energy vibronic sub-band of the phosphorescence spectrum at 77 K in 2-methyltetrahydrofuran.

The redox properties of polymers were examined using cyclic voltammetry (CV; Model: EA161 eDAQ). Thin films were coated on a Pt plate using chloroform (CHCl₃) as a solvent. The electrolyte solution was 0.10-M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in freshly dried acetonitrile. The reference electrode was Ag/AgCl and the counter electrode was Pt wire (0.5 mm in diameter). The scan rate was 50 mV s⁻¹.

Solvent Resistance of Photo-Crosslinked Films

Commercially available microscope slides were used as substrates for examining the solvent resistance of photocured films. The slides were cut to the size 2.5×2.5 cm² and cleaned by ultrasonic treatment in distilled water, acetone, chloroform, and 2-propanol, in sequence. The polymers, **P(mCP-Ox)-I**, **-II**, and **-III** were dissolved in dry chlorobenzene (10 mg mL⁻¹) and mixed with 2 wt % of the photoinitiator [4-[(2-hydroxytetradecyl)oxy]phen-yl]phenyliodonium hexafluoro antimonate just before spin-coating. 30-nm-thick polymer layers were fabricated, which were spin-coated on the glass substrates at ambient conditions. The films were then cured with UV light ($\lambda_{max} = 254$ nm) irradiation at 150 °C for 30–60 s. The solubilities of the photo-cured films were examined by comparing UV spectra of the film samples before and after rinsing with THF, which is a good solvent for the pristine polymers.

Measurement of Performances of Blue Ph-PLEDs

When fabricating blue Ph-PLEDs via solution processing, PEDOT:PSS, FIrpic, and 3,3'-[5'-[3-(3-pyridinyl)phenyl] [1,1':3',1"-terphenyl]-3,3"-diyl]bispyridine (TmPyPB) were employed as HIL, blue dopant, and electron transport materials, respectively. The fabricated multilayered Ph-PLEDs have the structure as follows: ITO/PEDOT:PSS (40 nm)/P(mCP-OX)-I or -II or -III (10 nm)/P(mCP-Ph):FIrpic (20 nm)/ TmPyPB (50 nm)/LiF (1.5 nm)/Al(100 nm). For fabricating devices A-E, water-soluble conducting PEDOT:PSS was spincoated onto the ITO-coated glass under argon, followed by spin coating the solution of P(mCP-Ox)-I, -II, or -III in chlorobenzene (0.5 wt %) onto PEDOT:PSS layer. Each photocrosslinkable polymer layer was exposed to the UV light $(\lambda_{\rm max} = 254 \text{ nm}, I = 40 \text{ mW cm}^{-2})$ for 30–60 s at 150 °C. The emitting layers made of **P(mCP-Ph)** containing FIrpic in a solution (0.5 wt %) of chlorobenzene were then spincoated onto the thoroughly dried and photocured P(mCP-Ox)-I, -II, and -III layers.

For fabricating hole-blocking and electron-transporting layers, TmPyPB (50 nm) was vacuum-deposited onto the emitting polymer layer. Finally, LiF (1.5 nm) and Al (100 nm) electrodes were deposited onto the TmPyPB layer. The final precise configurations of the fabricated devices are as follows:

Device A: ITO/PEDOT:PSS/P(mCP-Ox)-I/P(mCP-Ph):10 wt % FIrpic/TmPyPB/LiF/Al;

Device **B**: ITO/PEDOT:PSS/**P(mCP-Ox)-II/P(mCP-Ph)**:10 wt % FIrpic/TmPyPB/LiF/Al;

Device **C**, **D**, **E**: ITO/PEDOT:PSS/**P(mCP-Ox)-III/P(mCP-Ph)**:10(**C**), 15(**D**), 20(**E**) wt % FIrpic/TmPyPB/LiF/Al.

The current density-voltage (*J*–*V*) and (*L*–*V*) data of the blue Ph-PLEDs were measured using Keithley 2635A and Minolta CS-100A meters, respectively. The PLED emission area was 4 mm² for all devices studied in this work. Electroluminescence (EL) spectra and CIE coordinates were obtained using a Minolta CS-1000 spectroradiometer.

RESULTS AND DISCUSSION

Synthesis

Monomer Synthesis

Monomers **7** and **9** were first prepared for use as photocrosslinkable hole-transporting copolymers and host polymer for blue dopant (FIrpic). The synthesis of monomer **1** (**7**) commenced with the metal-halogen exchange of 1,3,5-tribromobenzene **1** using *n*-butyllithium in diethyl ether. The thermally unstable monolithiated intermediate was transformed to aldehyde **2** (76%).²⁸ The 3,5-dibromobenzyl alcohol **3**



SCHEME 1 Synthesis of monomer 1 (7) and monomer 2 (9).

was obtained by the reduction of **2** with sodium borohydride (93%).²⁹ Subsequent protection of compound **3** by TBDMS-Cl, followed by C—N coupling using the Buchwald-Hartwig amination protocol furnished mCP-containing **5** (70%). The TBDMS protecting group of **5** was deprotected in the presence of hydrochloric acid in THF. Finally, monomer **1** was



SCHEME 2 Synthesis of hole-transport P(mCP-Ox)s and host polymer P(mCP-Ph).

	Feeding Ratio (<i>m</i> : <i>n</i>)	Calculation Ratio (<i>m</i> : <i>n</i>)	<i>M</i> _n (kDa)	PDI	<i>T</i> g (°C)	<i>T</i> _d (°C)
P(mCP-Ox)-I	1:1	1:0.75 ^a	22	1.86	130	387
P(mCP-Ox)-II	1:2	1:1.45 ^a	23	1.85	137	387
P(mCP-Ox)-III	1:4	1:3.06 ^a	23	1.84	140	388
P(mCP-Ph)	1:3	1:2.15 ^b	10	1.76	148	381

TABLE 1 Physical Properties of P(mCP-Ox) and P(mCP-Ph) Copolymers

 $^{\rm a}$ Calculated from the ratio between integrated areas at 3.0–3.4 ppm and at 8.0 ppm assigned to the protons in $^{1}{\rm H}$ NMR spectrum.

^b Calculated from the ratio between integrated areas at 4.0–4.5 ppm and at 8.0 ppm in ¹H NMR spectrum.

prepared by the reaction of compound **5** with 4-vinyl benzyl chloride under basic conditions (72%). Oxetane-functionalized monomer **2** (**9**) was also synthesized by a one-step etherification. (3-Methyloxetan-3-yl)methanol (**8**) was coupled with 4-vinyl benzyl chloride, yielding the desired 3-methyl-3-(((4-vinylbenzyl)oxy)methyl)oxetane (**9**) in the presence of sodium hydride (Scheme 1).³⁰

A simple synthetic route to the photo-crosslinkable hole-conducting P(mCP-Ox) copolymers and host P(mCP-Ph) copolymer are depicted in Scheme 2. Each P(mCP-Ox) copolymer was prepared by the radical polymerization of monomer 1 and monomer 2 with varied monomer feeding compositions. After polymerization was complete, the reaction mixture was precipitated in methanol. The crude polymer was then purified by Soxhlet extraction with acetone and chloroform, successively. The resulting products were obtained as white powder in 42-65% yield. P(mCP-Ox) copolymers with three different monomer-feeding ratios were synthesized in order to investigate the influence of oxetane content on physical and device performance. The molecular weights and resultant copolymer compositions using the two monomers are shown in Table 1. The resultant molar ratios of the two monomers incorporated into the P(mCP-Ox) copolymers were calculated from the ratio between the integrated areas at 3.0-3.4 ppm assigned to the protons of the oxymethylene groups in oxetane moiety and at 8.0 ppm assigned to the protons in aromatic ring. Similarly, the molar ratio of P(mCP-Ph) was also calculated from the ratio between the

integrated areas at 4.0-4.5 ppm assigned to the oxymethylene protons in monomer **1** and at 8.0 ppm assigned to the protons in aromatic ring.

The molecular weights of polymers were determined by GPC with polystyrene as a standard and THF as an eluent. The number average molecular weights (M_n) of **P(mCP-Ox)-I**, **-II**, **-III**, and **P(mCP-Ph)** were determined to be 22, 23, 23, and 10 kDa with polydispersites (PDIs) of 1.86, 1.85, 1.84, and 1.76, respectively. The polymers were found to have good self-film-forming properties and were highly soluble in various organic solvents such as chloroform, xylene, dichloromethane, chlorobenzene, and THF.

Thermal Analysis

The thermal properties of the polymers were characterized by means of TGA and DSC; results of the analyses are illustrated in Figures 1 and 2, respectively. TGA measurements at a heating rate of $10 \,^{\circ}$ C min⁻¹ under nitrogen revealed that the polymers had good thermal stabilities and an enhanced onset decomposition temperature (381–388 °C) (Fig. 1). DSC measurements were performed at a heating (cooling) scan rate of 10 (and $-10) \,^{\circ}$ C min⁻¹ under nitrogen, with the highest temperature limited to being below the decomposition temperature (Fig. 2). The **P(mCP-Ox)** copolymers exhibited no crystalline isotropic transitions in the range of 25–250 °C, whereas glass transition temperatures (T_g) were observed at 130, 137, and 140 °C for **P(mCP-Ox)-I, -II**, and **-III**, respectively. **P(mCP-Ox)-III** showed the highest T_g among the three copolymers. The higher



FIGURE 1 TGA curves of (a) P(mCP-Ox)-I (1), -II (2), and -III (3), and (b) P(mCP-Ph).



 80
 100
 120
 140
 160
 180
 200
 100
 120
 140
 160
 180

 Temperature(°C)
 Temperature (°C)

-1

FIGURE 2 DSC curves of (a) P(mCP-Ox)-I (1), -II (2), and -III (3), and (b) P(mCP-Ph).

composition of mCP unit in **P(mCP-Ox)-III** is thought to contribute to the enhancement of polymer rigidity. In addition, the $T_{\rm g}$ of **P(mCP-Ph)** was determined to be 148 °C (Table 1).

UV-Vis Absorption and PL Spectroscopy

-6

Figure 3 shows UV-vis absorption, PL, and low-temperature PL spectra of the polymers synthesized in the present. The absorption spectra of **P(mCP-Ox)-I**, **-II**, and **-III** in the solution and film states are shown in Figure 3(a,b). The solution and film samples exhibited absorption maxima between 294

and 296 nm, which was attributed to the incorporated carbazole units. The large optical bandgaps (E_g) of **P(mCP-Ox)-I**, **-II**, and **-III**, as determined from the absorption onset wavelengths, were estimated to be very similar, at 3.56, 3.55, and 3.53 eV, respectively.

Similarly, the absorption spectra of P(mCP-Ph) in the solution and film states are shown in Figure 4(b). The solution and film samples exhibited absorption maxima between 294 and 395 nm, which were attributed to the



FIGURE 3 UV-vis absorption spectra of (a) P(mCP-Ox)-I (1), -II (2), and -III (3) solutions, and (b) film samples, (c) PL spectra of the three copolymers at 77 K.

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FIGURE 4 UV-vis absorption and PL spectra of the (a) P(mCP-Ph) solution, and (b) film samples: (i) absorption spectrum; (ii) PL spectrum at 25 °C; (iii) PL spectrum at 77 K.

incorporated carbazole units and intermolecular interactions. The optical bandgap (E_g) of **P(mCP-Ph)**, as determined from the absorption onset wavelength, was estimated to be 3.54 eV.

PL emission peaks of the **P(mCP-Ox)** and **P(mCP-Ph)** films were observed at 392–413 nm at room temperature. Lowtemperature PL measurements of **P(mCP-Ox)** [Fig. 3(c)] and **P(mCP-Ph)** [Fig. 4(a)] were also carried out at 77 K to calculate $E_{\rm T}$ from the first phosphorescent emission peak. The triplet energy was obtained from the first vibronic transition of the red-shifted phosphorescence spectrum. The $E_{\rm T}$ values of the copolymers were 3.00 eV ($\lambda_{\rm em} = 413$ nm) identically, which is high enough to permit energy transfer from host polymer to blue phosphorescent FIrpic dopant. The high $E_{\rm T}$ of mCP was fully maintained despite being tethered to the styrene polymer backbone. Therefore, **P(mCP-Ox)** and **P(mCP-Ph)** may be suitable for use as the hole transporting material and host material for blue Ph-PLEDs, respectively.

Electrochemical Analysis

Electrochemical behaviors of copolymers **P(mCP-Ox)-I**, **-II**, **-III**, and **P(mCP-Ph)** were investigated by CV measurements. The oxidation potentials were measured relative to ferrocene, which was used as internal standard. The oxidation potentials of **P(mCP-Ox)-I**, **-II**, **-III**, and **P(mCP-Ph)** were measured to be 0.98, 0.88, 0.85, and 0.96 V, respectively. The HOMO levels of **P(mCP-Ox)-I**, **-II**, **-III**, and **P(mCP-Ph)** were

determined to be -5.78, -5.68, -5.65, and -5.76 eV, respectively (Table 2). To determine the lowest unoccupied molecular orbital (LUMO) level, the oxidation potential from CV was combined with the optical energy bandgap obtained from the absorption edge in the absorption spectrum. The LUMO level of **P(mCP-Ox)-I**, **-II**, and **-III**, and **P(mCP-Ph)** were determined to be -2.22, -2.13, -2.12, and -2.22 eV, respectively. The energy levels of **P(mCP-Ox)-I**, **-II**, and **-III**, and **-II**, and **-III**, and **-**

Solvent Resistance of the Photo-Crosslinked Polymers

P(mCP-Ox) copolymers are readily soluble in common organic solvents such as toluene, chloroform, and THF. After UV-light illumination to induce crosslinking, thin-films solubilities were significantly altered, and the thin films became insoluble in THF and halogenated hydrocarbon solvents. Photo-crosslinking of thin films composed of **P(mCP-Ox)**s was induced via cationic polymerization, which is commonly used for the ring-opening reaction of cyclic ethers such as oxirane and oxetane moieties.

The commercially available photoinitiator [4-[(2-hydroxytetradecyl)oxy]phenyl] phenyl-iodonium hexafluoroantimonate, which can undergo photolysis at 210–254 nm was added to initiate the crosslinking process. During ultraviolet (UV) illumination, this photoinitiator decomposes via a multiple-step

TABLE 2 Optical and Electrochemical Properties of P(mCP-Ox) and P(mCP-Ph) Copolymers

	λ ^{abs.} m	λ ^{abs.} max (nm)		λ ^{em.} _{max} (nm)				Energy Level (eV)	
	Sol.	Film	Sol.	Film	$E_{\rm T}$ (eV)	$\lambda_{ m cut~off}$ (nm)	E_{g}^{opt} (eV)	HOMO ^c	LUMO ^d
P(mCP-Ox)-I	294	296	351	392	3.00	348 ^a , 348 ^b	3.56 ^a , 3.56 ^b	-5.78 ^b	-2.22 ^b
P(mCP-Ox)-II	294	295	351	406	3.00	348ª, 349 ^b	3.56 ^a , 3.55 ^b	-5.68 ^b	-2.13 ^b
P(mCP-Ox)-III	294	296	351	413	3.00	348ª, 351 ^b	3.56 ^a , 3.53 ^b	-5.65^{b}	-2.12 ^b
P(mCP-Ph)	294	395	351	368	3.00	348 ^a , 350 ^b	3.56 ^a , 3.54 ^b	-5.76^{b}	-2.22 ^b

^a Absorption measured in CH₂Cl₂.

^b Absorption measured in solid state film.

^c Calculated from the oxidation potentials.

 $^{\rm d}$ Calculated from the HOMO energy levels and $E_{\rm g}{}^{\rm opt}$



FIGURE 5 Absorption spectral analysis of (a) P(mCP-Ox)-I, (b) -II, and (c) -III films: (i) before UV irradiation (254 nm); UV-exposure time (ii) 5 s, (iii) 30 s, (iv) 60 s, then rinsed in THF; *Inset: Patterned image of P(mCP-Ox)-I film, (d) Solvent resistance of P(mCP-Ox)-I (1), -II (2), and -III (3) versus UV-exposure time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanism to generate protons, which open the oxet ane ring and start the polymerization reaction. $^{\rm 13-22}$

UV-vis absorption spectroscopy was employed to examine the efficiency of the crosslinking process (Fig. 5). Changes in solubility of the **P(mCP-Ox)-I** and **-II** films before and after UV irradiation were investigated at 150 °C (Table 3). The photopatterned image was illustrated as an inset of Figure 5(a).

The films were rinsed with THF after UV irradiation for a fixed irradiation timed (t = 5, 30, and 60 s) and the spectra were recorded again. The polymers **P(mCP-Ox)-I** and **-II** gave similar results; absolute solvent resistivity was observed for both polymers with 2 wt % of the photoinitiator at a curing temperature of 150 °C for 30 s. In contrast, it was observed that **P(mCP-Ox)-III** required much longer curing times (t = 60 s) at the same temperature as compared to **P(mCP-Ox)-I** and **-II** (t = 30 s), because of its lower oxetane monomer concentration.

Characterization of Blue Ph-PLEDs

To explore the possibility of the newly synthesized polymers for hole transport material and host material in blue Ph-PLEDs, **P(mCP-Ox)-I**, **-II**, **-III**, and **P(mCP-Ph)** were applied to multilayered blue Ph-PLED. Figure 6 illustrates the alignment of the energy levels of all the layers comprising the PLEDs. PEDOT:PSS was used as a hole injection layer. P(mCP-Ox) and TmPyPB were used as hole- and electron- transporting layer.

The high triplet energy, high-lying HOMO-level good filmforming ability, and especially fast conversion to insoluble layer for **P(mCP-Ox)-I, -II**, and **-III** make them good candidates for solution-processed hole transport materials for blue Ph-PLEDs. Figure 7 shows the performances of blue

TABLE 3 Influence of Curing Time on the Solvent Resistivity of

 Crosslinked Layer P(mCP-Ox)

	Solvent Resistivity = (Abs ₁ /Abs _o) × 100				
Polymer	5 s	30 s	60 s		
P(mCP-Ox)-I	82	98	100		
P(mCP-Ox)-II	81	96	100		
P(mCP-Ox)-III	10	40	100		

Abs₀: absorbance at 341 nm after UV exposure.

Abs₁: absorbance at 341 nm after rinsing the film in THF.





FIGURE 6 (a) Energy-level alignment of multilayered blue Ph-PLED; molecular structures of (b) P(mCP-Ox), (c) P(mCP-Ph), (d) TmPyPB, (e) Flrpic, and (f) cationic photoinitiator. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Ph-PLEDs **A**, **B**, and **C** made of different hole-transport polymers, **P(mCP-Ox)**s at a fixed concentration of FIrpic (10 wt % into **P(mCP-Ph)**).

The current density-voltage-luminance (*J*-*V*-*L*), current efficiency-luminance (CE-*L*), power efficiency-luminance (PE-*L*), and external quantum efficiency-luminance (EQE-*L*)



FIGURE 7 Device performance of soluble blue Ph-PLED: (a) J-V-L (inset: EL spectra of the three devices), (b) CE-L, (c) PE-L, and (d) EQE-L characteristics of blue Ph-PLED (i.e., device A: circle, device B: triangle, device C: square). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Device	HTL Polymer	HTL Thickness (nm)	Flrpic (wt %)	V _{turn on} (V)	CE _{max} (cd/A)	PE _{max} (Im/W)	EQE _{max} (%)	CIE _{max} (<i>x, y</i>)
А	P(mCP-Ox)-I	10	10	6.0	1.66	0.55	0.96	0.17, 0.34
В	P(mCP-Ox)-II	10	10	6.5	1.71	0.56	1.03	0.18, 0.35
С	P(mCP-Ox)-III	10	10	6.0	5.34	2.24	2.18	0.16, 0.33
D	P(mCP-Ox)-III	10	15	6.0	8.75	3.93	2.55	0.17, 0.34
E	P(mCP-Ox)-III	10	20	6.0	2.69	1.09	0.90	0.17, 0.34

TABLE 4 Devices Performance of Blue Ph-PLED

values of three devices are well illustrated in Figure 8(a–c), respectively.

The turn-on voltages for these devices were typical for FIrpicdoped PLEDs and were in the range of 6.0–6.5 V.³¹ Moderately low turn-on voltages were observed even for crosslinked **P(mCP-Ox)**. The EL spectra of all three devices containing **P(mCP-Ph)** host are almost identical without any emission from the host and or adjacent layers. The EL spectral results indicate that complete energy transfer from **P(mCP-Ph)** to FIrpic took place upon electrical excitation, and charge carriers and excitons are well confined in the emitting zone.

Among three devices A, B, and C, the device C exhibited much better maximum device efficiencies. It might be attributed to better hole transport property of P(mCP-Ox)-III. As was shown in Table 4, the improved performance can be attributed to the charge balance of electron and hole fluxes in emitting zone because the internal quantum efficiency of the Ph-PLED device is directly related to the balance of electrons and holes in the device.^{32,33} Device **C** bearing 10 wt % FIrpic, shows a turn-on voltage of 6.0 V at a luminance of 1.0 cd m^{-2} , a maximum CE of 5.34 cd A^{-1} , a maximum PE of 2.24 lm W^{-1} , and maximum EQE of 2.18%, with CIE coordinate of (0.16, 0.33). As the device C showed better performance than the devices A and B, dopant-concentration dependence of the device efficiency was investigated further. The concentration of FIrpic dopant was varied from 10 to 20 wt % into P(mCP-Ph). In comparison, the device D bearing 15 wt % FIrpic, exhibited the maximum CE of 8.75 cd A^{-1} , maximum PE of 3.93 lm W^{-1} , and maximum EQE of 2.55%, with CIE coordinate of (0.17, 0.34). On the while, the device **E** bearing 20 wt % FIrpic, exhibited a CE of 2.69 cd A^{-1} , a PE of 1.09 lm W^{-1} , and EQE of 0.90%, with CIE coordinate of (0.17, 0.34), which are less efficient than the devices C and D. It might be attributed to triplet-triplet annihilation.³¹⁻³⁴ Therefore, we could suggest that P(mCP-Ox)-III containing the highest concentration of hole-transporting, mCP unit has a great potential for enhance hole injection/transport properties.

CONCLUSIONS

In conclusion, hole-transport copolymers incorporating oxetane moieties as photo-crosslinking units and blue host polymers incorporating styrene units have been synthesized and characterized. The molar ratio of **P(mCP-Ox)** having the same photo-crosslinking unit was varied. Insoluble crosslinked films were obtained by UV-irradiation and the solvent resistance was investigated by UV-vis absorption spectroscopy. The photo-crosslinkable hole-affine polymers allowed for the fabrication and investigation of multilayer Ph-PLED devices by the spin-coating method. The fabricated blue Ph-PLEDs based on **P(mCP-Ox)-I**, **-II**, **-III**, and **P(mCP-Ph)** showed reasonable performances under an applied electric field. In particular, **P(mCP-Ox)-III**, which contains the highest composition of hole-transport (mCP) unit, exhibited the best performance as a hole transport material in blue Ph-PLED, possibly by inducing more balanced charge carriers and carrier recombination in the EML.

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