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Copolymers containing pendant styryltriphenylamine and carbazole groups: Synthesis, optical, electrochemical properties and its blend with Ir(*ppy*)$_3$

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ABSTRACT

A series of vinyl copolymers (**PVKST12**–**PVKST91**) and homoploymer **PVST** containing pendant hole-transporting 4-(4-oxystyryl)triphenylamine (12–100 mol%) and carbazole chromophores were synthesized by radical copolymerization and employed as host for Ir(*ppy*)$_3$ phosphor to tune emission color. They were characterized using the ^{1}H NMR, FT-IR, absorption and photoluminescence spectra, elemental analysis, GPC, cyclic voltammetric and thermal analysis (DSC, TGA). Their weight-average molecular weights (M_w) and decomposition temperatures (T_d) were 1.46–5.68 × 10^4 and 356–399 °C, respectively. The HOMO levels of **PVKST12**–**PVKST91** and **PVST**, estimated from the onset oxidation potentials in cyclic voltammograms, were −5.40 to −5.14 eV, which are much higher than −5.8 eV of the conventional host poly(9-vinylcarbazole) (**PVK**) owing to high hole-affinity of the 4-(4-oxystyryl)triphenylamine groups. Therefore, copolymers **PVKST** are effective in reducing hole-injection barrier between the PEDOT:PSS and emitting layer. Electroluminescent devices [ITO/PEDOT:PSS/**PVKST**:Ir(*ppy*)$_3$:PBD/BCP/Ca/Al] using the hole-transporting **PVKST** as host were fabricated to tune the emission color. Their EL spectra showed a major emission at 515 nm and a minor peak at 435 nm attributed to Ir(*ppy*)$_3$ and 4-(4-oxystyryl)triphenylamine, respectively. The C.I.E. 1931 coordinates shift from (0.29, 0.61) for **PVK** to (0.33, 0.42) for **PVST** with an increase in 4-(4-oxystyryl)triphenylamine content.

1. Introduction

Organic phosphorescent light-emitting diodes (LEDs) based on heavy-metal complexes from small organic molecules [1–5] and polymers [6–12] have attracted great attention currently due to their potential in attaining higher efficiency, resulting from emission of both singlet and triplet excitons. Recently, many electroluminescent devices consisting of iridium [2], platinum [13], and ruthenium [14] metal complexes have been investigated. The presence of heavy metal complexes enhances phosphorescence because the strong spin–orbit coupling leads to rapid intersystem crossing (ISC) and short triplet state lifetime [15]. Baldo fabricated high efficiency LEDs by doping phosphorescent complex tris(2-phenylpyridine) iridium [Ir(*ppy*)$_3$] into small-molecular host material 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) [4]. Polymer materials have also been expected as potential host in optoelectronic devices due to the advantages of good processability, simple fabrication by solution processes, and good thermal stability. Phosphorescent LEDs fabricated using a carbazole-based polymer, poly(9-vinylcarbazole) (**PVK**), as the host material for the phosphorescent Ir(*ppy*)$_3$ dopant by simple solution process were reported [6–8]. Jou et al. reported that single emission layer LEDs composing of CBP and poly[(9,9-dioctyl-fluorenyl-2,7-diyl)-*alt*-(9-hexyl-3,6-carbazole)] (PF-9HK) showed lower energy barrier for hole injection into emitting layer [16]. Mechanistically, for efficient Förster energy transfer to phosphorescent dopant, the spectral overlap between the photoluminescence (PL) band of the host material and the absorption band of the phosphorescent dopant is indispensable.

Although several kinds of phosphorescent polymers possessing both host units and heavy-metal complexes have been synthesized and discussed [17–20], complicated synthetic procedures and high cost impede their commercial development. Blending is one of the adaptable methods to circumvent this difficulty, although there still remain some intrinsic problems such as aggregation of the phosphor, phase separation, and inefficient energy transfer [21–23]. In addition, accurate composition control over the hosts and phosphors is much easier for the blend system, compared with phosphorescent polymers consisting of both host units and heavy-metal complexes. Kim et al. reported that the blend of host PVK, fully conjugated blue emitter, and green phosphor Ir(PDPP)$_3$ showed variable emission spectra depending on blend composition [24]. However, in fully conjugated polymers

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the effective conjugation length is in fact statistically distributed that leads to segments with different energy gaps and broader emission color. Therefore, confinement of the conjugation into a well-defined length is very important and one of the most successful strategies to obtain pure emission color. Polymers carrying isolated luminescent functional groups in their side chains exhibited good control over the conjugation length [25–27].

In this work, we prepared five new copolymers (**PVKST**) containing pendant carbazole and 4-(4-oxystyryl)triphenylamine chromophores, from which different emission colors were obtained by doping with green phosphor Ir(*ppy*)$_3$ owing to varied HOMO energy levels. The luminescent blend films of these host copolymers and green phosphor [Ir(*ppy*)$_3$] were prepared by casting from their chlorobenzene solution. Composition-dependent photoluminescence (PL) and electroluminescence (EL) spectral properties of the blends were investigated in detail.

2. Experimental

2.1. Materials and characterization

Poly(9-vinylcarbazole) (**PVK**) and 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) were purchased from Aldrich and used without further purification. Iridium complexes Ir(*ppy*)$_3$ were purchased from American Dye Source (ADS). 4-Vinylbenzyl chloride (**6**) was distilled under reduced pressure to remove inhibitor before use. The precursor copolymers (**PCB**) were prepared by free radical polymerization of 4-vinylbenzyl chloride (**6**) and 9-vinylcarbazole (**7**) using AIBN as an initiator. The copolymers (**PVKST**) were prepared by the Williamson condensation of the corresponding precursor copolymers (**PCB**), respectively, with the hole-affinitive monomer 4-(4-(diphenylamino)styryl)phenol (**5**) [28,29]. AIBN was purified by re-crystallizing twice from ethanol and dried at room temperature under vacuum. Other reagents were of commercial sources and used without further purification. The solvents were dried by the conventional procedures. All new compounds were identified by ^{1}H NMR, FT-IR, and elemental analysis (EA). The ^{1}H NMR spectra were recorded with a Bruker AMX-400 MHz FT-NMR, and chemical shifts are reported in ppm using tetramethylsilane (TMS) as an internal standard. The FT-IR spectra were measured using a Fourier transform infrared spectrometer, model 7850 from Jasco. The elemental analysis was carried out on a Heraus CHN-Rapid elemental analyzer. The molecular weight and molecular weight distribution of the polymers were determined by a gel permeation chromatography (GPC) using chloroform as eluent and mono-disperse polystyrenes as calibration standard. The thermogravimetric analysis (TGA) of the polymers was performed under nitrogen atmosphere at a heating rate of 20 °C/min using a PerkinElmer TGA-7 thermal analyzer. Thermal transition properties of the polymers were measured using a differential scanning calorimeter (DSC), PerkinElmer DSC-7, under nitrogen atmosphere at a heating rate of 10 °C /min.

Absorption spectra were measured with a Jasco V-550 spectrophotometer and PL spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer. The cyclic voltammograms were recorded with a voltammetric analyzer (model CV-50W from BAS) at room temperature under nitrogen atmosphere. The measuring cell comprised a glassy carbon as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum wire as the auxiliary electrode, which were immersed in 0.1 M acetonitrile solution of (n-Bu)$_4$NClO$_4$. The scan rate was 100 mV/s. The energy levels were calculated using the value −4.8 eV of ferrocene (FOC) with respect to vacuum level, which is defined as zero [30].

2.2. Fabrication and optoelectronic measurements of electroluminescent devices

The EL device configuration was ITO/PEDOT:PSS/**PVK** or **PVST** or **PVKST** series:Ir(*ppy*)$_3$:PBD/BCP/Ca (50 nm)/Al (100 nm), in which PBD was added to improve the electron transport [12]. The PLEDs were fabricated on pre-cleaned indium tin oxide (ITO) substrates with a sheet resistance of 14 Ω per square. The poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was first coated onto ITO glass as the hole-injection layer and annealed at 150 °C for 0.5 h in a dust-free atmosphere. The emitting layer, **PVK** or **PVST** or **PVKST** series:PBD (40 wt%) doped with Ir(*ppy*)$_3$, was spin-coated onto the PEDOT:PSS layer from its solution in chlorobenzene. Finally, the calcium and aluminum cathode were deposited successively onto the polymer film via thermal evaporation under *ca.* 2×10^{-6} Torr. The film thicknesses of emissive layers were about 77–104 nm as measured by α-step 500 profiler. The EL spectra and current density–voltage–luminance (*J*–*V*–*L*) characteristics of the devices were measured using a power supply (Keithley 2400) and a fluorescence spectrophotometer (Ocean Optics usb2000).

2.3. Monomer synthesis (Scheme 1)

*2.3.1. 4-Bromotriphenylamine (**2**)*

A mixture of triphenylamine (**1**: 2.455 g, 10 mmol) and NBS (1.959 g, 11 mmol) in 40 mL dry DMF under nitrogen were stirred at 100 °C for 3 h. After cooling to room temperature, the mixture was poured into distilled water and extracted with chloroform. The organic layer was dried with anhydrous magnesium sulfate and vacuum concentrated. The crude product was purified by re-crystallizing from ethanol to get white crystal of **2**.

Yield: 79%. FT-IR (KBr pellet, cm^{-1}): 3058, 3034, 1581, 1483, 1313, 1274, 1174, 1073, 1007, 817, 751, 693. ^{1}H NMR (Acetone, ppm): 7.45–7.28 (m, 6H, Ar H), 7.09–6.9 (m, 8H, Ar H). ^{13}C NMR (400 MHz, CDCl$_3$): δ 147.38, 147.35, 132.13, 129.50, 124.80, 124.50, 123.49, 114.08. Anal. Calcd. for $C_{18}H_{14}NBr$: C, 66.68%; H, 4.35%; N, 4.32%. Found: C, 66.44%; H, 4.25%; N, 4.20%.

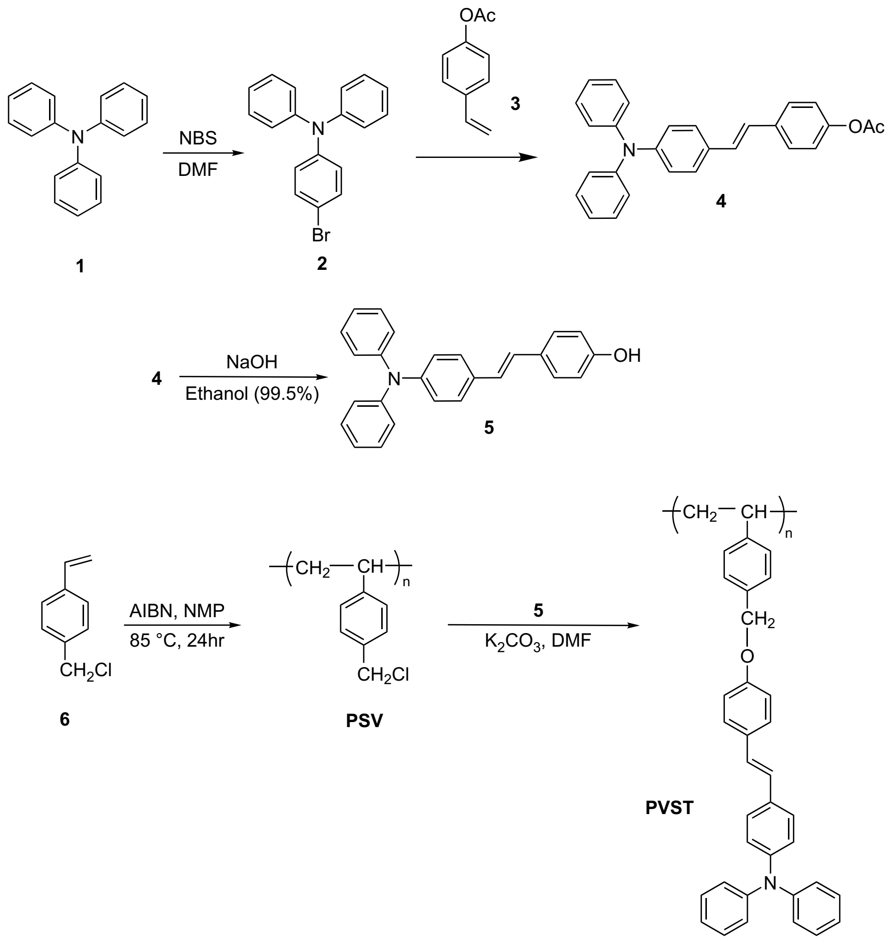
*2.3.2. 4-(4-(Diphenylamino)styryl)phenyl acetate (**4**)*

A mixture of **2** (2.210 g, 6.8 mmol), 4-acetoxystyrene (**3**: 1.353 g, 8.3 mmol), Pd(OAc)$_2$ (37 mg, 0.2 mmol), triethylamine (1.940 g, 19.2 mmol), and tri-*o*-tolylphosphine (0.230 g, 0.8 mmol) in 30 mL dry DMF under nitrogen was stirred at 100 °C for 60 h. After cooling to room temperature, the mixture was poured into distilled water and extracted with chloroform. The organic layer was dried with anhydrous magnesium sulfate and vacuum concentrated. The crude product was purified by column chromatography (chloroform/*n*-hexane = 2/1) and then re-crystallized from ethanol/acetone to provide yellow crystal of **4**.

Yield: 64%. FT-IR (KBr pellet, cm^{-1}): 3085, 3061, 3035, 3000 (aromatic C–H stretching), 1588, 1508, 1487 (aromatic C═C), 1762 (–C═O–), 970, 910 (–CH═CH$_2$). ^{1}H NMR (DMSO, ppm): 7.59–6.93 (m, 18H, Ar H, 2H, Ar–C$\underline{\text{H}}$═C$\underline{\text{H}}$–Ar), 2.26 (s, 3H, CH$_3$). ^{13}C NMR (500 MHz, DMSO): δ 169.37, 149.82, 147.14, 146.96, 135.18, 131.44, 129.75, 128.22, 127.79, 127.32, 126.09, 124.30, 123.44, 123.19, 122.23, 21.02. Anal. Calcd. for $C_{28}H_{23}NO_2$: C, 82.94%; H, 5.72%; N, 3.45%. Found: C, 82.60%; H, 5.69%; N, 3.43%.

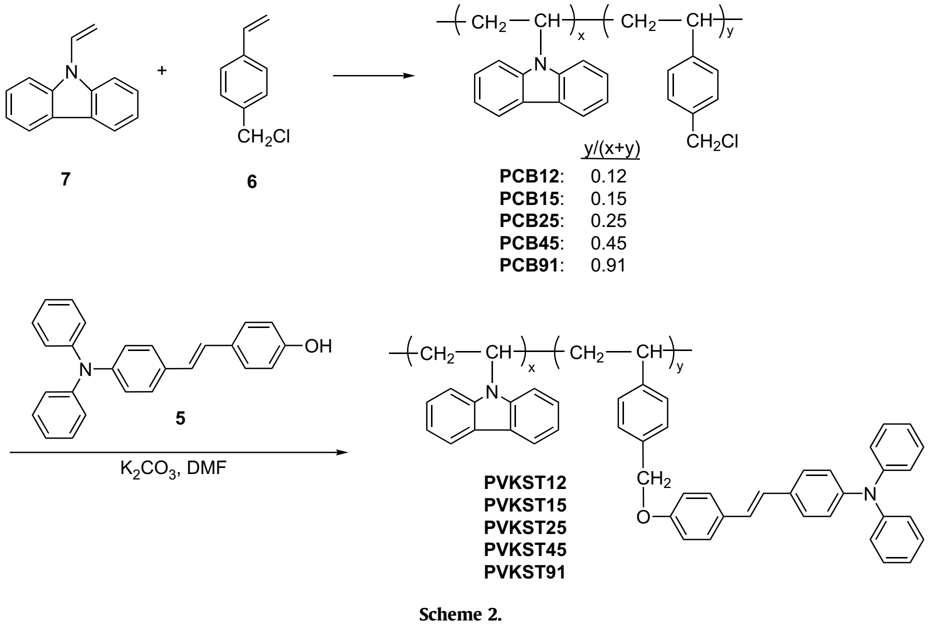
*2.3.3. 4-(4-(Diphenylamino)styryl)phenol (**5**)*

A mixture of **4** (1.0 g, 2.5 mmol) and sodium hydroxide (0.97 g, 24.2 mmol) in 80 mL ethanol (99.5%) under nitrogen were stirred at 90 °C for 4 h. After cooling to room temperature, the mixture was poured into distilled water and neutralized by HCl. The crude product was filtered, washed with water and dried in vacuum oven to provide yellow powder of **5**.



Scheme 1.

Yield: 97% (mp: 187–188 °C). FT-IR (KBr pellet, cm^{-1}): 3508, 3461 (–OH), 3088, 3055, 3032, 3001 (aromatic C–H stretching), 1588, 1510, 1484 (aromatic C=C), 966, 835 (–CH=CH$_2$). ^{1}H NMR (Acetone, ppm): 7.47–6.81 (m, 18H, Ar H, 2H, Ar–C$\underline{H}$=C$\underline{H}$–Ar). ^{13}C NMR (500 MHz, Acetone): δ 158.10, 148.60, 147.67, 133.50, 130.22, 130.15, 128.50, 128.08, 127.94, 125.91, 125.04, 124.58, 123.86, 116.41. Anal. Calcd. for $C_{26}H_{21}NO$: C, 85.92%; H, 5.82%; N, 3.85%. Found: C, 85.77%; H, 5.88%; N, 3.84%.



Scheme 2.

2.4. *Homopolymer synthesis (Scheme 1)*

Precursor polymer (**PSV**) was prepared by the free radical polymerization of 4-vinylbenzyl chloride (**6**) using AIBN as an initiator. The synthetic procedures and characterization of **PSV** are described as follows: a mixture of 4-vinylbenzyl chloride (**6**: 1.503 g, 9.8 mmol) and AIBN (31 mg) was dissolved in 6 mL dry NMP and then added to a polymerization tube fitted with a magnetic stirring bar. The mixture was degassed by four freeze–evacuate–thaw cycles and the tube was sealed under vacuum. The mixture was stirred at 85 °C for 24 h. After pouring into methanol, the appearing precipitates were collected by centrifugal sedimentation and then purified by extracting with methanol for 24 h using a Soxhlet extractor. Thus-obtained polymer was further purified by being dissolved in $CHCl_3$ and re-precipitated from methanol several times. The product was collected by centrifugal sedimentation and dried under vacuum to give a white powder of **PSV**.

Yield: 76%. FT-IR (KBr pellet, cm^{-1}): 3049, 3022, 3014 (aromatic C–H stretching), 2919, 2849 (C–H stretching), 673 (–C–Cl–). ^1H NMR ($CDCl_3$, ppm): 7.28–6.28 (m, 4H, Ar H), 4.51 (s, Ar–CH_2–Cl), 1.99–1.25 (m, 3H, –CH–CH_2–). Anal. Calcd. for $(C_9H_9Cl)_n$: C, 70.83%; H, 5,94%. Found: C, 71.38%; H, 6.05%.

2.4.1. *Poly(*N*-(4-(4-(4-vinylbenzyloxy)styryl)phenyl)-*N*-phenylbenzenamine) (**PVST**)*

PVST was prepared by the Williamson condensation of the corresponding precursor polymer (**PSV**) with 4-(4-(diphenylamino)styryl)phenol (**5**). The **PSV** (0.104 g, 0.68 mmol) was dissolved in dry DMF (29 mL), adding with compound **5** (0.739 g, 2.03 mmol) and K_2CO_3 (0.338 g, 2.44 mmol). The mixture was stirred at 120 °C for 24 h under nitrogen atmosphere. After pouring into methanol, the appearing precipitates were collected by centrifugal sedimentation and then purified by extracting with methanol for 24 h using a Soxhlet extractor. Thus obtained polymer was further purified by being dissolved in $CHCl_3$ and re-precipitated from methanol several times. The product was collected by centrifugal sedimentation and dried under vacuum to give a yellowish powder of **PVST**.

FT-IR (KBr pellet, cm^{-1}): 3080, 3056, 3025, 3026, 3006 (aromatic C–H stretching), 2919, 2861 (C–H stretching), 1589, 1507, 1488 (aromatic C=C), 962, 694 (–C=C–). ^1H NMR ($CDCl_3$, ppm): 7.26–6.56 (m, 24H, Ar H), 4.81 (s, Ar–CH_2–O), 2.03–1.12 (m, 3H, –CH–CH_2–) Anal. Calcd. for $(C_{35}H_{29}NO)_n$: C, 87.65%; H, 6.09%; N, 2.92%. Found: C, 86%; H, 6.15%; N, 2.9%.

Table 1
Polymerization results and characterizations of **PCB**, **PSV**, **PVST**, and **PVKST**.

Polymer	Composition[a] (*x*, *y*)	Yield (%)	M_n[b] (×10^4)	M_w[b] (×10^4)	PDI[b]	T_d[c] (°C)	T_g (°C)
PCB12	(0.88, 0.12)	73	0.58	1.08	1.86	359	–[d]
PCB15	(0.85, 0.15)	90	0.62	1.18	1.90	374	–[d]
PCB25	(0.75, 0.25)	54	0.51	0.94	1.84	370	–[d]
PCB45	(0.55, 0.45)	45	0.50	0.77	1.54	355	–[d]
PCB91	(0.09, 0.91)	80	0.51	0.82	1.61	363	–[d]
PSV	(0, 100)	76	1.18	2.10	1.78	366	–[d]
PVKST12	(0.88, 0.12)	–	0.76	1.46	1.92	389	–[d]
PVKST15	(0.85, 0.15)	–	0.83	1.61	1.94	399	–[d]
PVKST25	(0.75, 0.25)	–	0.98	1.65	1.68	356	186
PVKST45	(0.55, 0.45)	–	1.17	2.16	1.85	380	171
PVKST91	(0.09, 0.91)	–	2.13	4.26	2.01	372	139
PVST	(0, 100)	–	3.05	5.68	1.86	386	139

[a] The compositions were estimated from ^1H NMR spectra and confirmed by elemental analysis.

[b] M_n, M_w, and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in $CHCl_3$.

[c] The temperature at 5% weight loss.

[d] No obvious T_g was observed in DSC thermograms.

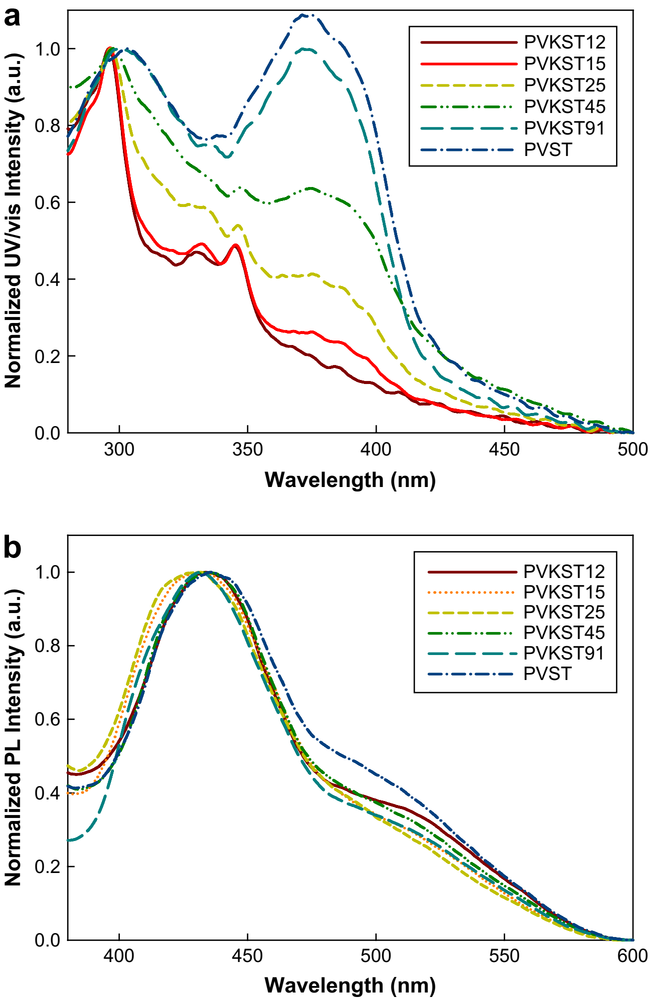


Fig. 1. (a) Absorption and (b) photoluminescence spectra of **PVKST12–PVKST91** and **PVST** films coated on quartz plate.

2.5. *Copolymer synthesis (Scheme 2)*

2.5.1. *Poly(9-vinylcarbazole-*co*-1-(chloromethyl)-4-vinylbenzene) (**PCB**)*

Precursor copolymers (**PCB**) were prepared by free radical polymerization of 9-vinylcarbazole (**7**) and 4-vinylbenzyl chloride

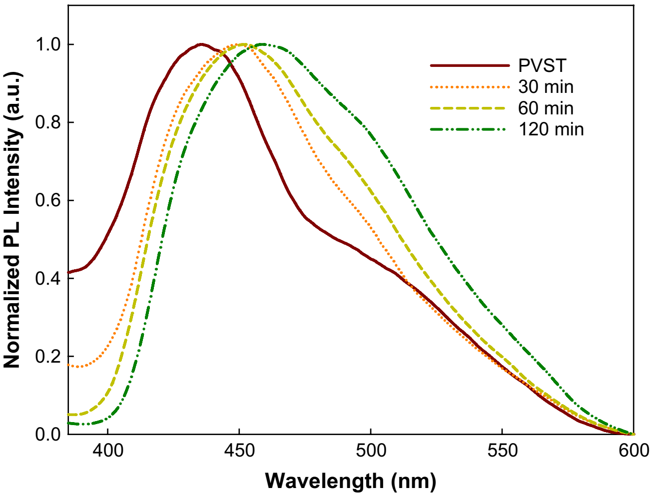


Fig. 2. PL spectra of the **PVST** film under thermal annealing at 160 °C for different time.

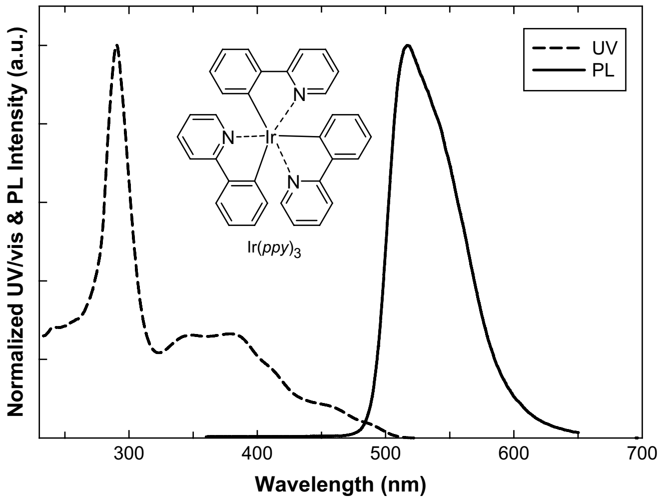


Fig. 3. Absorption and photoluminescence spectra of Ir(*ppy*)$_3$ films.

(**6**) as shown in Scheme 2. For example, the synthetic procedures and characterization of **PCB12** are described as follows: a mixture of 9-vinylcarbazole (**7**: 1.353 g, 7.0 mmol), 4-vinylbenzyl chloride (**6**: 0.107 g, 0.7 mmol), AIBN (29 mg), and 6 mL dry NMP was added to a polymerization tube fitted with a magnetic stirring bar. The mixture was degassed by four freeze–evacuate–thaw cycles and the tube was sealed under vacuum. The mixture was stirred at 75 °C for 24 h. After precipitation from methanol, the appearing precipitates were collected by centrifugal sedimentation and then purified by extracting with methanol for 24 h using a Soxhlet extractor. Thus-obtained polymer was further purified by being dissolved in $CHCl_3$ and re-precipitated from methanol several times. The product was collected by the centrifugal sedimentation and dried under vacuum to give white powder of **PCB12**.

Yield: 73%. FT-IR (KBr pellet, cm^{-1}): 3053, 3017 (aromatic C–H stretching), 2967, 2928 (C–H stretching), 745, 718 (–C–Cl–). ^1H NMR ($CDCl_3$, ppm): 7.72–6.45 (m, Ar H), 4.38 (s, Ar–CH_2–Cl), 2.54–1.25 (m, –CH–CH_2–). Anal. Calcd. for $(C_{13.4}H_{10.76}N_{0.88}Cl_{0.12})_n$: C, 85.5%; H, 5.72%; N, 6.55%. Found: C, 85.12%; H, 5.9%; N, 6.75%.

Other precursor copolymers (**PCB15**, **PCB25**, **PCB45**, **PCB91**) were prepared by the procedures analogous to those employed in the synthesis of **PCB12**.

2.5.1.1. ***PCB15***. Yield: 90%. FT-IR (KBr pellet, cm^{-1}): 3.50, 3019 (aromatic C–H stretching), 2956, 2927 (C–H stretching), 748, 724 (–C–Cl–). ^1H NMR ($CDCl_3$, ppm): 8.05–4.90 (m, Ar H), 4.37 (s, Ar–CH_2–Cl), 2.50–1.08 (m, –CH_2–CH–). Anal. Calcd. for $(C_{13.25}H_{10.7}N_{0.85}Cl_{0.15})_n$: C, 85.06%; H, 5.72%; N, 6.37%. Found: C, 84.62%; H, 5.79%; N, 6.61%.

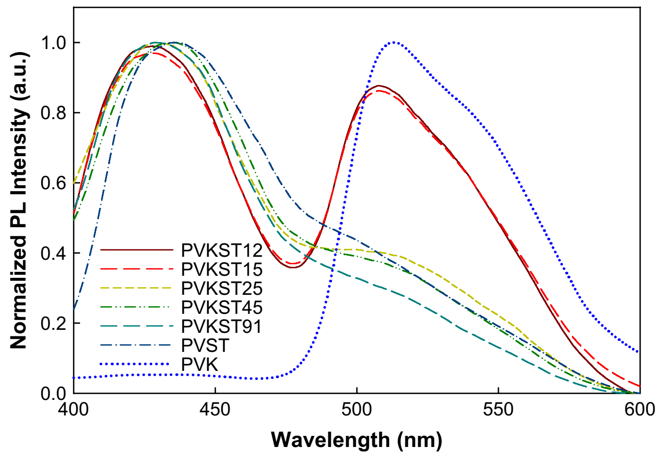


Fig. 4. PL spectra of the copolymers **PVKST** series, **PVST** and **PVK** films doped with 4 wt% Ir(*ppy*)$_3$ (with $\lambda_{ex} = 330$ nm).

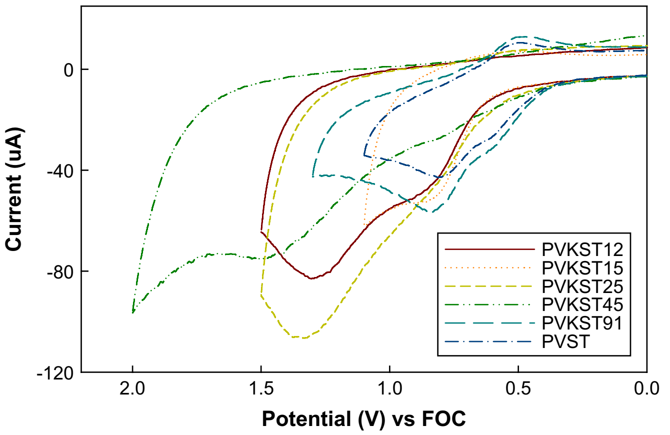


Fig. 5. Cyclic voltammograms of copolymers **PVKST** and homopolymer **PVST** coated on ITO glass electrode; scan rate: 100 mV/s.

2.5.1.2. ***PCB25***. Yield: 54%. FT-IR (KBr pellet, cm^{-1}): 3054, 3019 (aromatic C–H stretching), 2963, 2927 (C–H stretching), 748, 719 (–C–Cl–). ^1H NMR ($CDCl_3$, ppm): 7.72–4.91 (m, Ar H), 4.37 (s, Ar–CH_2–Cl), 2.51–1.27 (m, –CH_2–CH–). Anal. Calcd. for $(C_{12.75}H_{10.5}N_{0.75}Cl_{0.25})_n$: C, 83.66%; H, 5.74%; N, 5.74%. Found: C, 83.07%; H, 5.95%; N, 5.58%.

2.5.1.3. ***PCB45***. Yield: 45%. FT-IR (KBr pellet, cm^{-1}): 3047, 3019 (aromatic C–H stretching), 2956, 2927 (C–H stretching), 748, 720 (–C–Cl–). ^1H NMR ($CDCl_3$, ppm): 8.03–6.75 (m, Ar H), 4.45 (s, Ar–CH_2–Cl), 2.41–1.16 (m, –CH_2–CH–). Anal. Calcd. for $(C_{11.75}H_{10.1}N_{0.55}Cl_{0.45})_n$: C, 80.67%; H, 5.78%; N, 4.4%. Found: C, 79.39%; H, 5.97%; N, 4.38%.

2.5.1.4. ***PCB91***. Yield: 80%. FT-IR (KBr pellet, cm^{-1}): 3086, 3047, 3019 (aromatic C–H stretching), 2924, 2850 (C–H stretching), 670 (–C–Cl–). ^1H NMR ($CDCl_3$, ppm): 8.09–6.27 (m, Ar H), 4.49 (s, Ar–CH_2–Cl), 2.21–0.91 (m, –CH_2–CH–). Anal. Calcd. for $(C_{9.45}H_{9.18}N_{0.09}Cl_{0.91})_n$: C, 72.63%; H, 5.88%; N, 0.91%. Found: C, 72.96%; H, 6.05%; N, 1.23%.

*2.5.2. Poly(9-vinylcarbazole-*co*-N-(4-(4-(4-vinylbenzyloxy)styryl)-phenyl)-N-phenylbenzenamine) (**PVKST**)*

Copolymers **PVKST** were prepared by the Williamson condensation of the corresponding precursor copolymers (**PCB**), respectively, with compound **5**. For example, the **PCB12** (0.304 g, 1.61 mmol) was dissolved in dry DMF (70 mL) and added with **5** (0.122 g, 0.34 mmol) and K_2CO_3 (0.273 g,

Table 2
Electrochemical data of **PVKST12**–**PVKST91** and **PVST**.

Polymer	$E_{onset\ (ox)}$ (V) versus FOC	E_{HOMO}[a] (eV)	E_{LUMO}[b] (eV)	E_g^{opt}[c] (eV)
PVKST12	0.60	−5.40	−2.37	3.03
PVKST15	0.59	−5.39	−2.37	3.02
PVKST25	0.56	−5.36	−2.38	2.98
PVKST45	0.44	−5.24	−2.27	2.97
PVKST91	0.36	−5.16	−2.20	2.96
PVST	0.34	−5.14	−2.19	2.95

[a] $E_{HOMO} = -e\ (E_{onset(ox)} + 4.8\ V)$.
[b] $E_{LUMO} = E_{HOMO} + E_g^{opt}$.
[c] Optical band gaps obtained from absorption spectra.

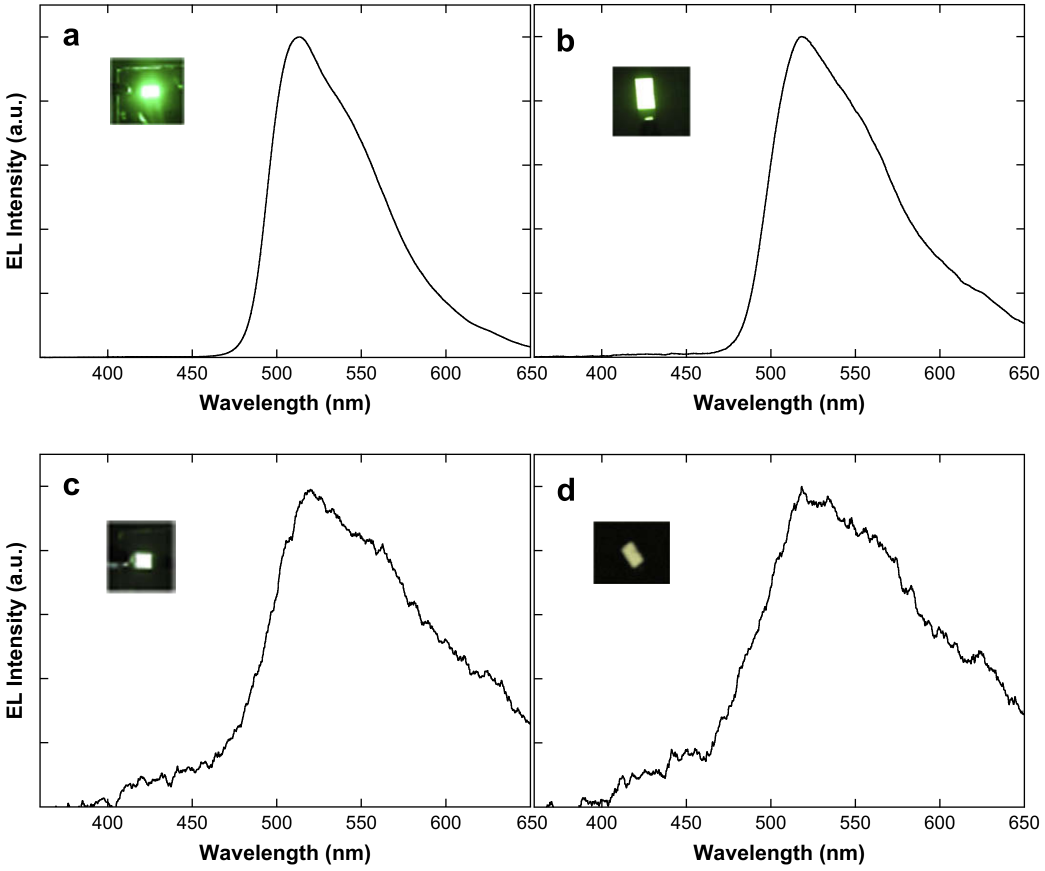


Fig. 6. EL spectra of the polymeric films doped with 4 wt% Ir(*ppy*)$_3$ (a) **PVK**; (b) **PVKST12**; (c) **PVKST45**; (d) **PVST**.

1.97 mmol). The mixture was stirred at 120 °C for 24 h under nitrogen atmosphere. After pouring into methanol, the appearing precipitates were collected by the centrifugal sedimentation and then purified by extracting with methanol for 24 h using a Soxhlet extractor. Thus-obtained polymer was further purified by being dissolved in $CHCl_3$ and re-precipitated from methanol several times. The product was collected by centrifugal sedimentation and dried under vacuum to give a dark purple solid of **PVKST12**.

FT-IR (KBr pellet, cm^{-1}): 3077, 3049, 3022 (aromatic C–H stretching), 2962, 2928 (C–H stretching), 1589, 1509, 1485 (aromatic C=C), 749, 718 (–C=C–). ^{1}H NMR ($CDCl_3$, ppm): 7.67–6.43 (m, Ar H), 4.85 (s, Ar–CH_2–O), 2.85–1.17 (m, –CH–CH_2–). Anal. Calcd. for $(C_{16.52}H_{14.92}NO_{0.12})_n$: C, 86.54%; H, 6.51%; N, 6.11%. Found: C, 85.64%; H, 5.86%; N, 6.32%.

Other copolymers (**PVKST15**, **PVKST25**, **PVKST45**, **PVKST91**) were prepared by the procedures analogous to those used in the synthesis of **PVKST12**.

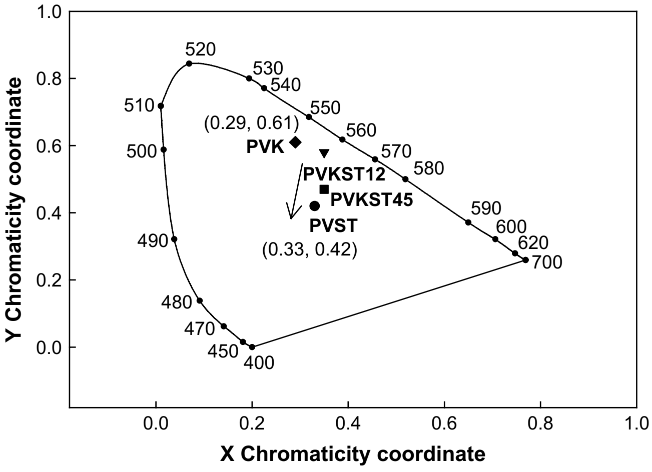


Fig. 7. The CIE 1931 diagram of the **PVK**, **PVKST12**, **PVKST45** and **PVST** films doped with 4 wt% Ir(*ppy*)$_3$.

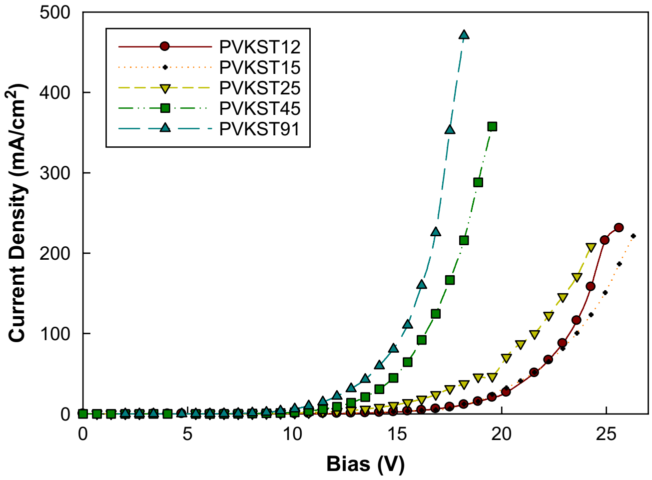


Fig. 8. The current density versus bias characteristics for the EL devices [ITO/PEDOT:PSS/**PVKST12**–**PVKST91**:Ir(*ppy*)$_3$:PBD/BCP/Ca/Al] prepared from **PVKST12**–**PVKST91** doped with 4 wt% Ir(*ppy*)$_3$.

2.5.2.1. ***PVKST15***. FT-IR (KBr pellet, cm^{-1}): 3077, 3053, 3022 (aromatic C–H stretching), 2959, 2925 (C–H stretching), 1594, 1509, 1482 (aromatic C=C), 745, 718 (–C=C–). ^1H NMR ($CDCl_3$, ppm): 7.69–6.42 (m, Ar H), 4.86 (s, Ar–CH_2–O), 2.55–0.88 (m, –CH–CH_2–). Anal. Calcd. for $(C_{17.15}H_{15.4}NO_{0.15})_n$: C, 86.62%; H, 6.48%; N, 5.89%. Found: C, 85.09%; H, 5.94%; N, 6.01%.

2.5.2.2. ***PVKST25***. FT-IR (KBr pellet, cm^{-1}): 3046, 3022 (aromatic C–H stretching), 2925, 2861 (C–H stretching), 1591, 1509, 1485 (aromatic C=C), 745, 718 (–C=C–). ^1H NMR ($CDCl_3$, ppm): 7.72–7.02 (m, Ar H), 4.82 (s, Ar–CH_2–O), 2.18–1.27 (m, –CH–CH_2–). Anal. Calcd. for $(C_{19.25}H_{17}NO_{0.25})_n$: C, 86.84%; H, 6.39%; N, 5.26%. Found: C, 85.15%; H, 5.9%; N, 5.31%.

2.5.2.3. ***PVKST45***. FT-IR (KBr pellet, cm^{-1}): 3053, 3022 (aromatic C–H stretching), 2925, 2861 (C–H stretching), 1592, 1509, 1488 (aromatic C=C), 749, 721, 694 (–C=C–). ^1H NMR ($CDCl_3$, ppm): 7.52–6.89 (m, Ar H), 4.79 (s, Ar–CH_2–O), 2.10–1.26 (m, –CH–CH_2–). Anal. Calcd. for $(C_{23.45}H_{20.2}NO_{0.45})_n$: C, 87.17%; H, 6.26%; N, 4.34%. Found: C, 86.3%; H, 6.03%; N, 4.27%.

2.5.2.4. ***PVKST91***. FT-IR (KBr pellet, cm^{-1}): 3080, 3056, 3025 (aromatic C–H stretching), 2919, 2861 (C–H stretching), 1589, 1507, 1488 (aromatic C=C), 749, 694 (–C=C–). ^1H NMR ($CDCl_3$, ppm): 7.26–6.83 (m, Ar H), 4.80 (s, Ar–CH_2–O), 1.61–1.25 (m, –CH–CH_2–). Anal. Calcd. for $(C_{33.11}H_{27.56}NO_{0.91})_n$: C, 87.62%; H, 6.07%; N, 3.09%. Found: C, 85.91%; H, 6.07%; N, 3.09%.

3. Results and discussion

3.1. Synthesis and characterization

The precursor copolymers **PCB** were prepared by the free radical polymerization of 9-vinylcarbazole (**7**) and 4-vinylbenzyl chloride (**6**) using AIBN as an initiator and NMP as solvent. The synthetic routes of the precursor **PSV** and homopolymer **PVST** are described in Scheme 1, whereas those of precursor copolymers **PCB** and copolymers **PVKST** are depicted in Scheme 2. The polymerization results and basic characterization of the polymers are summarized in Table 1. The weight-average molecular weights (M_w) of **PCB12**, **PCB15**, **PCB25**, **PCB45**, and **PCB91**, determined by GPC using polystyrene as standard, were 1.08×10^4, 1.18×10^4, 0.94×10^4, 0.77×10^4, and 0.82×10^4, respectively. Copolymers **PVKST** synthesized from the corresponding precursor copolymers **PCB** via the Williamson condensation, i.e. condensation of pendant benzyl chloride of **PCB** with reactive phenol group of 4-(4-(diphenylamino)styryl)phenol (**5**). The weight-average molecular weights (M_w) of **PVKST12**, **PVKST15**, **PVKST25**, **PVKST45** and **PVKST91** were 1.46×10^4, 1.61×10^4, 1.65×10^4, 2.16×10^4 and 4.26×10^4, respectively. The weight-average molecular weights of **PVKST** (1.46–4.26×10^4) are much higher than those of the corresponding precursor copolymers (0.82–1.18×10^4) due to the attachment of 4-(4-oxystyryl)triphenylamine as pendant groups. Moreover, the increase in molecular weights depends upon the contents of benzyl chloride side groups, i.e. the higher the contents the greater the molecular weight enhancement.

The composition of **PCB**, **PSV**, **PVST**, and **PVKST** have been estimated from their ^1H NMR spectra and confirmed by the elemental analysis. The actual compositions of the copolymers (**PCB**, **PVKST**) differ slightly from the feed comonomer compositions. For example, the feed molar ratio of **7** to **6** is 10/1 in the preparation of **PCB12**; however, the molar ratio (x/y) in the resulting copolymer is 88/12. This is due to different copolymerization reactivity of the two vinyl monomers, i.e. monomer **6** is more reactive than monomer **7**. The chemical shift at 4.45 ppm attributed to benzyl protons (e_1) in precursor copolymer **PCB45** shifts completely to 4.78 ppm (e_2) in **PVKST45**, indicating complete condensation of the side benzyl chloride with **5**. The copolymers exhibited moderate thermal stability with thermal decomposition temperature (at 5% weight loss) being 356–399 °C (Table 1). The char yields of **PVKST12**–**PVKST91** and **PVST** are 5.5, 14.0, 22.9, 23.3, 31.2 and 31.3 wt%, respectively, indicating that the thermal resistance is enhanced with an increase in the content of 4-oxystyryltriphenylamine pendant groups.

3.2. Photophysical properties

Fig. 1(a) shows the absorption spectra of films cast from copolymers **PVKST** and homopolymer **PVST**. The first (303 nm) and second absorption (375 nm) peaks of **PVST** are attributed to π–π^* and n–π^* transition, respectively. The absorption peaks of **PVKST12** locate at 295, 330, 344 and 375 nm. Compared with the absorption spectrum of **PVK**, [32] the absorption peaks at 295, 330, and 344 nm are attributed to carbazole and the peak at 375 nm is originated from the absorption of 4-(4-oxystyryl)triphenylamine unit (**PVST**). Moreover, the absorption intensity at 375 nm enhances gradually with an increase in 4-(4-oxystyryl)triphenylamine content. As shown in Fig. 1(b), the PL spectra of **PVST** film shows an emission peak at 435 nm and a shoulder around 510 nm. The latter emission shoulder was not observed in dilute solution and can be attributed to the formation of the inter- or intramolecular interactions (aggregation and/or excimer). In order to confirm that the main PL band around 510 nm is resulted from the formation of molecular interactions, emission of the **PVST** film was traced after thermal annealing at 160 °C (higher than T_g of **PVST**) for 30, 60, 120 min as shown in Fig. 2. The emission intensity at 510 nm enhances gradually with increasing time of thermal treatment, suggesting that the 510 nm band can be ascribed to the formation of molecular interactions. This indicates that the emission peak around 510 nm is attributed to excimer emission.

Fig. 3 shows the absorption and PL spectra of Ir(*ppy*)$_3$ films cast from chlorobenzene. The absorption spectrum of Ir(*ppy*)$_3$ film shows strong absorption at 290 nm originated from the ligand-centered π–π^* transition and weaker absorptions at 340–380 and 460 nm attributed to the singlet metal-to-ligand charge transfer (^{1}MLCT) and triplet metal-to-ligand charge transfer (^{3}MLCT) transition, respectively [31]. The PL spectrum of Ir(*ppy*)$_3$ film shows an emission peak at 517 nm, which is exclusively attributed to ^{3}MLCT transition [30]. The probability of Förster energy transfer from host to phosphor can be expected by the degree of spectral overlap between donor's PL band and acceptor's absorption band. As shown in Figs. 1(b) and 3, the PL band of copolymers **PVKST** overlaps greatly with the absorption band of the MLCT transition in Ir(*ppy*)$_3$, indicating that efficient energy transfer from copolymers **PVKST** to Ir(*ppy*)$_3$ would occur.

Fig. 4 shows the PL spectra of the blend films [**PVKST** and **PVST** doped with 4 wt% Ir(*ppy*)$_3$] spin-coated from chlorobenzene solution. The PL spectrum of **PVK** doped with Ir(*ppy*)$_3$ is almost the same as that of Ir(*ppy*)$_3$, indicating that the excitation energy is transferred completely from the host (**PVK**) to the phosphor [Ir(*ppy*)$_3$] during photo-excitation. The efficient Förster energy transfer is owing to spectral overlap between the PL band of **PVK** and the absorption band of Ir(*ppy*)$_3$. On the contrary, the PL spectra of **PVKST**:Ir(*ppy*)$_3$ show an emission peak at *ca.* 435 nm attributed to the emission of **PVST** and a shoulder or peak at *ca.* 515 nm originated from the emission of Ir(*ppy*)$_3$. Moreover, the emission intensity at 435 nm enhances gradually with an increase in **PVST** content. The emission of **PVST** at 435 nm is owing to incomplete photo-excited energy transfer to Ir(*ppy*)$_3$ due to less overlap between absorption spectrum of **PVST** and PL band of Ir(*ppy*)$_3$.

3.3. Electrochemical measurements

The HOMO energy levels of **PVKST12**–**PVKST91** and **PVST** films were estimated from their cyclic voltammograms using the equation $E_{\mathrm{HOMO}} = -(E_{\mathrm{onset(ox)}} + 4.8)$ eV, where $E_{\mathrm{onset(ox)}}$ is the onset oxidation potential relative to the ferrocene/ferrocenium couple. Fig. 5 shows the cyclic voltammograms (CV) of **PVKST12**–**PVKST91** and **PVST** films coated on a glassy carbon electrode in anodic scan, with the corresponding electrochemical data summarized in Table 2. The onset oxidation potential of **PVKST12**–**PVKST91** and **PVST** are at 0.60, 0.59, 0.56, 0.44, 0.36 and 0.34 eV, respectively. The HOMO energy level of **PVKST12**–**PVKST91** and **PVST** calculated from their onset oxidation potentials are −5.40, −5.39, −5.36, −5.24, −5.16 and −5.14 eV, respectively, which are higher than that of **PVK** (−5.8 eV). This seems to be attributed to stronger hole-affinity of pendant 4-(4-oxystyryl)triphenylamine groups. Accordingly, the energy barrier for hole injection from the PEDOT:PSS to emitting layers can be effectively reduced. Moreover, the HOMO levels of the polymers (**PVKST12**–**PVKST91** and **PVST**) vary with their compositions. The LUMO energy levels of **PVKST12**–**PVKST91** and **PVST**, calculated from the HOMO energy levels and the optical energy gaps (E_g^{opt}), are −2.37, −2.37, −2.38, −2.27, −2.20 and −2.19 eV, respectively.

3.4. Electroluminescent characteristics of the EL devices

Fig. 6 shows the EL spectra of the blend films [copolymers **PVKST** and homopolymer **PVST** doped with 4 wt% Ir(ppy)$_3$], wherein the inset shows the device images under operation. The device configuration is ITO/PEDOT:PSS/**PVKST** or **PVST**:Ir(p-py)$_3$:PBD/Ca/Al. The CIE 1931 coordinate of **PVK**:Ir(ppy)$_3$ system without **PVST** is (0.29, 0.61), which is part of green region.[1] With the increase of **PVST** content (**PVKST12** and **PVKST45**), new luminescence appears at 430–480 nm, which can be attributed to the emission of pendant 4-(4-oxystyryl)triphenylamine chromophores. The corresponding CIE 1931 coordinates are shown in Fig. 7, in which they are (0.29, 0.61), (0.35, 0.58), (0.35, 0.47), and (0.33, 0.40) for **PVK**, **PVKST12**, **PVKST45**, and **PVST** devices, respectively. With an increase in 4-(4-oxystyryl)triphenylamine content the emission color shifts from green to yellowish-white. Fig. 8 shows the plots of current density versus bias for the EL devices of the blend films. There exists a clear tendency of decreased operating voltage with an increase of 4-(4-oxystyryl)triphenylamine content, suggesting that the hole injection barrier between the PEDOT:PSS and emitting layers is reduced due to the addition of the chromophores.

4. Conclusion

A series of vinyl copolymers **PVKST** and homopolymer **PVST** containing pendant carbazole and 4-(4-oxystyryl)triphenylamine groups (12–100 mol%) were successfully prepared from precursor polymers **PCB**. The high molecular weight **PVKST** ($M_w = 14600$–42600, PDI = 1.68–2.01) exhibited good solubility in common organic solvents such as toluene, chloroform, THF, and 1,1,2,2-tetrachloroethane. The emission color of their EL devices doped with 4 wt% Ir(ppy)$_3$ phosphor shifted from green to yellowish-white with an increase in 4-(4-oxystyryl)triphenylamine content. Copolymers **PVKST** and homopolymer **PVST** showed higher HOMO level (−5.40 to −5.14 eV) relative to **PVK** (−5.8 eV), leading to reduced operating voltage in their EL devices due to enhanced hole injection.

Acknowledgments

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[1] (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)