Polymer-Based Tris(2-phenylpyridine)iridium Complexes

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ABSTRACT: A series of *fac*-Ir(ppy)$_3$ complex functionalized poly(styrene)s and poly(*N*-vinylcarbazole)-*co*-poly(styrene)s were synthesized. The emission wavelength of all polymers could be readily tuned from 550 to 515 nm by reducing the linkage of the Ir complex to the polymer backbones from a Schiff base to an amine. The reduced polymers retained the photophysical properties of the corresponding small molecule *fac*-Ir(ppy)$_3$, including transient absorption behaviors, high emission quantum yields (0.12−0.23), and long excited-state lifetimes (963−1221 ns). These results clearly indicate that the polymer backbones do not interfere with the photophysical properties of the pendant *fac*-Ir(ppy)$_3$ chromophore but endow solution processability to these materials for potential use in light-emitting devices and emissive display technology.

Introduction

In this contribution, we describe the synthesis and photophysical characterization of a new class of polymer-supported iridium complexes based on poly(*N*-vinylcarbazole)-*co*-poly(styrene) copolymers and facial iridium tris-2-phenylpyridine (*fac*-Ir(ppy)$_3$). Cyclometalated Ir(III) complexes are outstanding phosphorescent materials for a wide variety of applications including organic light-emitting diodes (OLEDs).[1−6] The strong spin−orbit coupling of the heavy Ir(III) ion results in the efficient intersystem crossing from the singlet to the triplet excited state, allowing Ir(III) complexes to utilize both singlet and triplet excitons for efficient electrophosphorescence at room temperature. Therefore, the internal quantum efficiency of such complexes can theoretically approach 100%.[7−9] For example, by using *fac*-Ir(ppy)$_3$ as the emissive layer in an OLED, an external quantum efficiency of more than 15% (approaching ca. 100% internal quantum efficiency) was achieved,[10] suggesting that the *fac*-Ir(ppy)$_3$ complex is the ideal choice for the fabrication of highly efficient phosphorescent OLEDs. However, the processing of such small organometallic complexes into large area displays is problematic and costly, often requiring high-vacuum deposition, thereby severely limiting the potential use of *fac*-Ir(ppy)$_3$ in applications and devices. The use of polymer-supported analogues of *fac*-Ir(ppy)$_3$ has been suggested to overcome this problem.

Polymer-based OLEDs are very attractive because the device can be fabricated using low cost and efficient wet processing techniques, such as spin-coating or screen or ink-jet printing.[11] Two basic classes of polymeric *fac*-Ir(ppy)$_3$ are imaginable: (i) *fac*-Ir(ppy)$_3$-doped polymers[12−14] and (ii) covalently supported polymeric *fac*-Ir(ppy)$_3$. The second approach in particular will allow for the formation of well-defined solid-state materials without the possibility of phase separation or dopant aggregation. Over the past 5 years, a limited number of contributions in the literature describe such a covalent approach. Polymer backbones that have been functionalized with heteroleptic Ir(III) complexes containing bis-cyclometalated ligands and an ancillary ligand such as acetylacetonate, bipyridine, or terpyridine include poly(fluorene)s,[15−18] poly(fluorene−carbazole) copolymers,[19] poly(*p*-phenylene)s,[20] poly(styrene)s,[21−23] poly(dimethylsiloxane),[24] and poly(ϵ-caprolactone)s.[11,25,26] However, in comparison to polymeric phosphorescent materials based on heteroleptic Ir(III) complexes, homoleptic Ir(III) complex-based polymers have rarely been reported. The only reports in the literature are by Burn, Samuel, and co-workers, who synthesized dendrimer-based homoleptic Ir(III) complexes,[27−32] and by us.[33] We reported recently the synthesis of *fac*-Ir(ppy)$_3$ and *mer*-Ir(ppy)$_3$ functionalized poly(norbornene)s via ring-opening metathesis polymerization that retained the optical properties of the phosphorescent small molecule analogues.[33] While both of these reports clearly demonstrate the potential of homoleptic Ir(III) complex-based materials, they do not employ commodity polymer backbones such as poly(styrene) or poly(acrylate). Herein, we report an efficient method to synthesize poly(styrene)-based phosphorescent materials by directly grafting homoleptic *fac*-Ir(ppy)$_3$ onto poly(*N*-vinylcarbazole)-*co*-poly(styrene)s and poly(styrene)s. The facial isomer of Ir(ppy)$_3$ is preferred over its meridional analogue because *fac*-Ir(ppy)$_3$ has a higher luminescent quantum yield ($\Phi = 0.40$)[34] than its meridional isomer ($\Phi = 0.036$).[35] Poly(*N*-vinylcarbazole)-*co*-poly(styrene)s and poly(styrene)s were chosen for the attachment of the *fac*-Ir(ppy)$_3$ because (i) poly(*N*-vinylcarbazole) (PVK) has been employed extensively as host for a variety of small molecule dye dopants in OLEDs[3,12−14,36,37] due to its outstanding hole-transporting properties[37] and its high-energy singlet excited state,[37] (ii) both PVK and poly(styrene) have excellent film-forming properties with high glass-transition temperatures, and (iii) poly(styrene) is widely used as a polymeric precursor for postpolymerization derivatization.[38]

Experimental Section

General Methods. All reagents were purchased either from Acros Organics or Aldrich and used without further purification unless otherwise noted. THF and CH$_2$Cl$_2$ were dried via passage through copper oxide and alumina columns. NMR spectra were taken using a 300 MHz Varian Mercury spectrometer. Gel-permeation chromatography (GPC) analyses were carried out using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector with methylene chloride as the eluant on American Polymer Standards 10 μm particle size, linear mixed bed packing

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columns. The GPC was calibrated using poly(styrene) standards. UV−vis absorption measurements were taken on a Shimadzu UV-2401 PC recording spectrophotometer. Emission measurements were acquired using a Shimadzu RF-5301 PC spectrofluorophotometer. Lifetime measurements were taken using a PTI model C-72 fluorescence laser spectrophotometer with a PTI GL-3300 nitrogen laser. Differential scanning calorimetry (DSC) data were collected using a Seiko model DSC 220C. Elemental analyses were taken using a Perkin-Elmer//CHNS/O analyzer 2400. Transient absorption spectra were carried out using a LKS60 flash photolysis system with a Quantel Brilliant B Nd:YAG laser pumped OPOTEK OPO at various delays following excitation at 420 nm. PSCl,[39] PSNH$_2$,[39] and *fac*-Ir(fppp)(ppy)$_2$[40] were prepared according to literature procedures.

Synthesis of Poly(9-vinylcarbazole)-*co*-poly(*p*-chloromethylstyrene), PCZCl. A solution of 9-vinylcarbazole (8.76 g, 45 mmol), *p*-chloromethylstyrene (0.77 g, 5 mmol), AIBN (0.20 g, 1 mmol), and THF (100 mL) was degassed for 1 h with argon and stirred for 24 h at 80 °C under an argon atmosphere. After cooling to room temperature, the reaction mixture was poured into an excess of methanol (800 mL). The resulting white solid was collected by filtration, washed with methanol to remove unreacted monomer, and dried in air to yield 7.61 g (80%) of the desired product. ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 1.14-2.50$ (broad m), 3.23 (broad s), 3.43 (broad s), 4.41 (broad s), 4.92 (broad s), 6.43 (broad s), 6.95 (broad s), 7.07 (broad s), 7.73 (broad s). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): $\delta = 35.5$, 48.1, 49.1, 49.9, 106.8, 110.5, 118.7, 120.1, 121.8, 123.7, 124.9, 128.8, 137.2, 139.9. GPC: $M_n = 4100$, $M_w = 7300$, and PDI = 1.78. Elem. Anal. Calcd for $(C_{135}H_{108}N_9Cl)_n$: C, 85.71; H, 5.75; Cl, 6.66. Found: C, 85.95; H, 5.99; Cl, 6.69.

Synthesis of Poly(9-vinylcarbazole)-*co*-poly(*p*-aminomethylstyrene), PCZNH$_2$. *Step 1*: A solution of PCZCl (1.0 g) and potassium phthalimide (1.8 g, 9.73 mmol) in DMF (20 mL) was heated at 100 °C for 12 h. A pink precipitate formed during the reaction. After cooling the reaction to room temperature, the precipitate was filtered off. The filtrate was precipitated into a large volume of methanol, and the resulting white solid was collected by filtration and washed with methanol. Yield: 0.92 g (87%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.90-1.75$ (broad), 2.57 (broad s), 3.24 (broad), 4.96 (broad m), 6.44 (broad m), 6.94 (broad s), 7.71 (broad s).

Step 2: A mixture of the phthalimide derivative (1.0 g) and hydrazine monohydrate (1.5 mL) in a mixed solvent (ethanol/THF, 1/1, v/v, 20 mL) was stirred at reflux for 24 h, during which time a white solid formed. The reaction mixture was filtered, and the filtrate was precipitated into a large volume of water. The resulting suspension was kept at 0 °C overnight. Filtration of the reaction mixture afforded the target amino polymer PCZNH$_2$ as a white solid. Yield: 0.65 g (69%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.91-1.75$ (broad m), 2.51 (broad s), 3.17 (broad s), 3.4 (broad s), 4.89 (broad m), 6.40 (broad m), 6.94 (broad s), 7.71 (broad m). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): $\delta = 23.6$, 25.1, 27.1, 29.6, 30.6, 34.3, 34.6, 35.5, 36.9, 37.1, 37.9, 39.1, 48.3, 49.2, 50.1, 66.8, 68.0, 107.4, 108.0, 110.3, 110.9, 113.4, 118.8, 120.1, 121.9, 123.7, 125.0, 126.3, 127.9, 136.4, 137.4, 137.7, 139.9.

Synthesis of PCZ(CH$_2$)$_4$NH$_2$. A mixture of PCZCl (3.0 g), 1,4-butanediamine (7.0 g), and KOH (3.0 g) was dissolved in 100 mL of THF and stirred at 80 °C for 48 h. The reaction was then poured into an excess of water (500 mL) and extracted twice with CH$_2$Cl$_2$ (2 × 100 mL). The organic layers were combined, washed five times with water, and dried over magnesium sulfate. The solution was concentrated and subsequently precipitated into an excess of MeOH (500 mL). A white solid was collected by filtration and dried to give 2.52 g (82%) of the target compound PCZ(CH$_2$)$_4$NH$_2$. ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 1.14-2.05$ (broad m), 2.49 (broad s), 2.70 (broad s), 3.40 (broad s), 4.89 (broad s), 6.42 (broad s), 6.91(broad s), 7.07 (broad s), 7.70 (broad s). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): $\delta = 35.6$, 36.6, 42.1, 49.9, 50.1, 51.2, 53.3, 107.4, 108.1, 110.4, 118.8, 120.1, 121.8, 123.7, 125.0, 125.2, 137.3, 139.9.

Synthesis of PS(CH$_2$)$_4$NH$_2$. The same procedure as described above for the preparation of PCZ(CH$_2$)$_4$NH$_2$ was employed. A mixture of PSCl (3.0 g), 1,4-butanediamine (2.5 g), and KOH (1.32 g) was used as starting materials. Yield: 2.90 g (92%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.91$ (broad s), 1.18 (broad s), 1.48 (broad s), 1.84 (broad s), 2.61 (broad s), 2.69 (broad s), 3.67 (broad s), 6.57 (broad m), 7.07 (broad s). ^{13}C NMR (75 MHz, CDCl$_3$) (ppm): $\delta = 26.7$, 27.2, 27.9, 30.5, 31.5, 40.4, 41.8, 43.8, 46.0, 125.6, 127.6, 127.9, 145.2.

Synthesis of PSN═CHIr(ppy)$_3$. A mixture of *fac*-Ir(fppy)(ppy)$_2$ (0.05 g), PSNH$_2$ (0.50 g), anhydrous Na$_2$SO$_4$ (1.50 g), and 40 mL of dry THF was stirred for 48 h at 80 °C. After cooling to room temperature, the reaction mixture was filtered. The filtrate was concentrated and then precipitated into a large volume of MeOH. The precipitate was collected by filtration to yield the product as a yellow solid. Yield: 0.53 g (96%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.90-1.85$ (broad m), 3.75 (broad s), 4.60 (broad s), 6.58 (broad m), 7.06 (broad s), 7.54 (broad s), 7.68 (broad s), 7.87 (broad s), 8.10 (broad s).

Synthesis of PS(CH$_2$)$_4$N═CHIr(ppy)$_3$. The same procedure as above for the preparation of PSN═CHIr(ppy)$_3$ was employed. A mixture of *fac*-Ir(fppy)(ppy)$_2$ (0.05 g) and PS(CH$_2$)$_4$NH$_2$ (0.50 g) was employed as starting materials. Yield: 0.49 g (89%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.91$ (broad m), 1.13 (broad s), 1.44 (broad s), 1.83 (broad s), 2.62 (broad s), 3.49 (broad s), 3.68 (broad s), 6.58 (broad m), 6.87−7.73 (broad m), 7.52 (broad s), 7.66 (broad s), 7.85 (broad s), 7.97 (broad s).

Synthesis of PCZN═CHIr(ppy)$_3$. The same procedure as above for the preparation of PSN═CHIr(ppy)$_3$ was employed. A mixture of *fac*-Ir(fppy)(ppy)$_2$ (0.02 g) and PCZNH$_2$ (0.20 g) was used as starting materials. Yield: 0.20 g (91%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.91-1.82$ (broad m), 2.52 (broad s), 3.22 (broad s), 3.45 (broad s), 4.85 (broad s), 6.43 (broad m), 6.95 (broad s), 7.71 (broad m).

Synthesis of PCZ(CH$_2$)$_4$N═CHIr(ppy)$_3$. The same procedure as above for the preparation of PSN═CHIr(ppy)$_3$ was employed. A mixture of *fac*-Ir(fppy)(ppy)$_2$ (0.02 g) and PCZ(CH$_2$)$_4$NH$_2$ (0.20 g) was used as starting materials. Yield: 0.18 g (85%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.91-1.82$ (broad m), 2.51 (broad s), 3.25 (broad s), 3.50 (broad s), 4.92 (broad s), 6.42 (broad s), 6.94 (broad s), 7.03 (broad s), 7.74 (broad s).

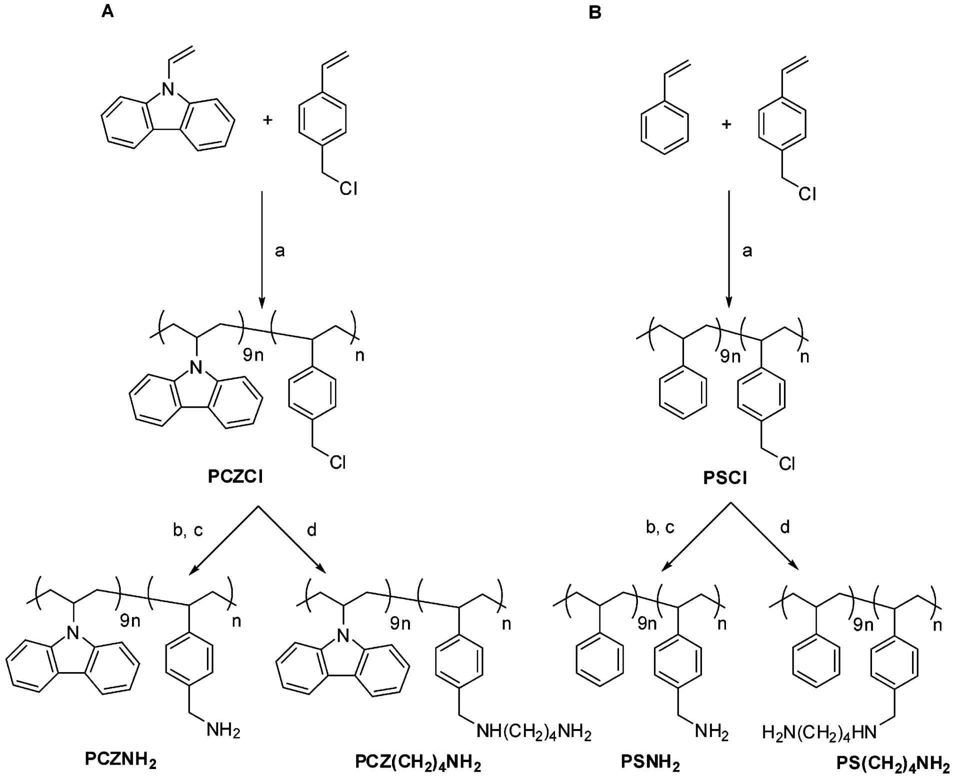
Synthesis of PSIr(ppy)$_3$. Under an argon atmosphere, PSN═CHIr(ppy)$_3$ (0.20 g) was dissolved in 25 mL of a mixture of THF and MeOH (3/1, v/v). Then NaBH$_4$ (0.02 g) was added, and the reaction was stirred for 12 h at room temperature. The reaction was quenched with 200 mL of water and extracted three times with 40 mL of methylene chloride. The combined organic layers were washed with water. After removal of the majority of the solvent, the residue was precipitated into a large volume of methanol. The precipitate was collected to yield the product as a light yellow solid (0.16 g, 80%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.90-1.85$ (broad m), 2.61 (broad s), 3.48 (broad s), 3.75 (broad s), 7.07 (broad s), 6.58 (broad s), 6.86−7.04 (broad, m), 7.53 (broad s), 7.66 (broad s), 7.86 (broad s), 7.96 (broad s).

Synthesis of PS(CH$_2$)$_4$Ir(ppy)$_3$. The same procedure as above for the preparation of PSIr(ppy)$_3$ was employed. Yield: 0.18 g (90%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.88-1.83$ (broad m), 2.62 (broad s), 3.70 (broad s), 6.60 (broad m), 6.84−7.10 (broad m), 7.52 (broad s), 7.61 (broad s), 7.87 (broad s).

Synthesis of PCZIr(ppy)$_3$. The same procedure as above for the preparation of PSIr(ppy)$_3$ was employed. Yield: 0.16 g (81%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.91-1.87$ (broad m), 2.54 (broad s), 3.45 (broad s), 4.85 (broad s), 6.40 (broad m), 6.91 (broad s), 7.68 (broad m).

Synthesis of PCZ(CH$_2$)$_4$Ir(ppy)$_3$. The same procedure as above for the preparation of PSIr(ppy)$_3$ was employed. Yield: 0.17 g (88%). ^{1}H NMR (300 MHz, CDCl$_3$) (ppm): $\delta = 0.95-1.82$ (broad m), 2.54 (broad s), 3.50 (broad s), 4.93 (broad s), 6.42 (broad s), 6.91 (broad s), 7.21 (broad s), 7.68 (broad s).

Scheme 1. Synthesis of NH_2-Functionalized Copolymers (A) Poly(*N*-vinylcarbazole)-*co*-poly(styrene)s and (B) Poly(styrene)-Based Copolymers[a]



[a] (a) AIBN, THF, 80 °C, 24 h; (b) potassium phthalimide, DMF, 100 °C, 12 h; (c) hydrazine monohydrate, THF/EtOH (1/1, v/v), reflux, 24 h; (d) $NH_2(CH_2)_4NH_2$, THF, KOH, 80 °C, 48 h.

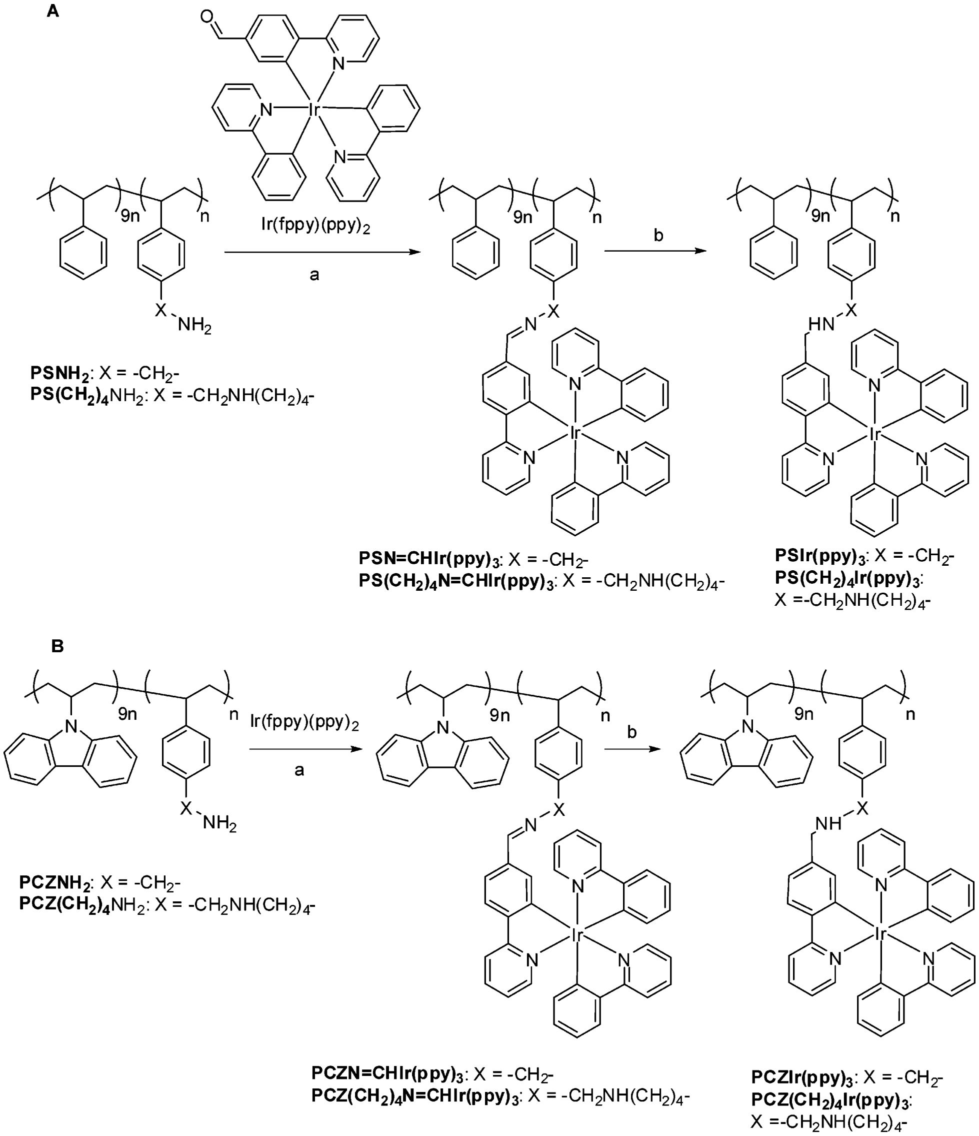
Results and Discussion

Synthesis. The synthetic routes toward *fac*-Ir(ppy)$_3$ functionalized poly(*N*-vinylcarbazole)-*co*-poly(styrene) copolymers and poly(styrene)s are outlined in Schemes 1 and 2. The synthesis toward the functionalized copolymers commences with the copolymerization of *p*-(chloromethyl)styrene with either *N*-vinylcarbazole or styrene via the free radical polymerization according to literature procedures.[39] Ratios of 9:1 of *N*-vinylcarbazole or styrene to *p*-(chloromethyl)styrene were copolymerized using AIBN as the initiator, yielding copolymers PCZCl ($M_n = 4100$; PDI = 1.78) and PSCl ($M_n = 6400$; PDI = 1.50), respectively. The chemical compositions of both copolymers were characterized by ^{1}H NMR and elemental analysis. The conversion of the chloromethylated copolymers to their amine analogues PCZNH$_2$ and PSNH$_2$ was carried out according to literature procedures,[39] by the treatment of the copolymers with potassium phthalimide followed by the reaction with hydrazine monohydrate to provide PCZNH$_2$ and PSNH$_2$ in quantitative yields. The amine functionalized copolymers containing a flexible butyl linker, PCZ(CH$_2$)$_4$NH$_2$ and PS(CH$_2$)$_4$NH$_2$, were obtained by reacting an excess of 1,4-diaminobutane with PCZCl and PSCl. Coupling of *fac*-bis(2-phenylpyridyl)-2-(4′-formylphenylpyridyl)iridium, *fac*-Ir(fppy)(ppy)$_2$,[40] with PCZNH$_2$, PCZ(CH$_2$)$_4$NH$_2$, PSNH$_2$, or PS(CH$_2$)$_4$NH$_2$ afforded the corresponding Schiff bases PCZN=CHIr(ppy)$_3$, PCZ(CH$_2$)$_4$N=CHIr(ppy)$_3$, PSN=CHIr(ppy)$_3$, and PS(CH$_2$)$_4$N=CHIr(ppy)$_3$ which were reduced to the corresponding amines using NaBH$_4$ to yield the desired *fac*-Ir(ppy)$_3$ functionalized polymers PCZIr(ppy)$_3$, PCZ(CH$_2$)$_4$Ir(ppy)$_3$, PSIr(ppy)$_3$, and PS(CH$_2$)$_4$Ir(ppy)$_3$ in quantitative yields, respectively. The glass-transition temperatures (T_g) of the obtained polymers are 3−5 °C higher than their analogous parent polymers, PSCl ($T_g \approx 100$ °C) and PCZCl ($T_g \approx 200$ °C).

Photophysical Characterization. Absorption Spectra. The UV−vis absorption spectra of molecular *fac*-Ir(ppy)$_3$, PS(CH$_2$)$_4$N=CHIr(ppy)$_3$, PS(CH$_2$)$_4$Ir(ppy)$_3$, PCZ(CH$_2$)$_4$N=CHIr(ppy)$_3$, and PCZ(CH$_2$)$_4$Ir(ppy)$_3$ are shown in Figures 1 and 2. Similar to the well-studied small molecule analogue *fac*-Ir(ppy)$_3$, the polymers have two main features in their absorption spectra. The strong absorption bands in the UV region from 235 to 320 nm are assigned as $\pi-\pi^*$ transitions stemming from the 2-phenylpyridine ligands or the carbazole, while the weak and broad absorption bands extending to around 500 nm are typical of metal-to-ligand charge-transfer (MLCT) transitions of *fac*-Ir(ppy)$_3$.[41] The corresponding polymers without a butyl linker PSN=CHIr(ppy)$_3$, PSIr(ppy)$_3$, PCZN=CHIr(ppy)$_3$, and PCZIr(ppy)$_3$ exhibit very similar absorption behaviors as their butyl linker-based counterparts.

Luminescent Properties. All *fac*-Ir(ppy)$_3$ functionalized polymers show strong photoluminescence in solution and the solid state (Table 1). The −N=CH− containing polymers of PSN=CHIr(ppy)$_3$, PS(CH$_2$)$_4$N=CHIr(ppy)$_3$, PCZ(CH$_2$)$_4$N=CHIr(ppy)$_3$, and PCZN=CHIr(ppy)$_3$ exhibit similar emission profiles with $\lambda_{max} \approx 550$ nm in solution and the solid state (Figure 3). Compared to their solution emission, the solid-state emission is slightly red-shifted (Table 1). The −N=CH− linker can significantly affect the emission properties as can be seen by the conversion of the aldehyde group of the starting material *fac*-Ir(fppy)(ppy)$_2$ ($\lambda_{max} = 600$ nm, Figure 3) to the corresponding Schiff base. The quantum yields of PSN=CHIr(ppy)$_3$, PS(CH$_2$)$_4$N=CHIr(ppy)$_3$, PCZN=CHIr(ppy)$_3$, and PCZ(CH$_2$)$_4$N=CHIr(ppy)$_3$ in deaerated CH$_2$Cl$_2$ are 0.04, 0.03, 0.02, and 0.05, respectively. These data are very close to that of the small molecule parent compound Ir(fppy)(ppy)$_2$ ($\Phi = 0.04$). The solution emission wavelength maxima of the −N=CH− containing polymers can be readily tuned from yellow to green-

Scheme 2. Synthesis of *fac*-Ir(ppy)$_3$-Functionalized Copolymers (A) Poly(styrene)-Based Copolymers and (B) Poly(*N*-vinylcarbazole)-*co*-poly(styrene)s[a]



[a] (a) CH_2Cl_2, Na_2SO_4, reflux 48 h; (b) $NaBH_4$, THF/MeOH (4/1, v/v), rt, 12 h.

yellow ($\lambda_{max} \approx 515$ nm) by simply reducing the $-N{=}CH-$ group to the corresponding amine $-NH_2CH_2-$ (Table 1). These photoluminescent results clearly indicated that the poly(styrene) and poly(9-vinylcarbazole)-*co*-poly(styrene) copolymers do not interfere with the luminescent properties of the pendant *fac*-Ir(ppy)$_3$. Figure 4 shows that the photoluminescence spectra of PS(CH$_2$)$_4$Ir(ppy)$_3$ and PCZ(CH$_2$)$_4$Ir(ppy)$_3$ are almost identical to that of the reference compound *fac*-Ir(ppy)$_3$. The quantum yields of PSIr(ppy)$_3$ ($\Phi = 0.23$), PS(CH$_2$)$_4$Ir(ppy)$_3$ ($\Phi = 0.19$), PCZIr(ppy)$_3$ ($\Phi = 0.12$), and PCZ(CH$_2$)$_4$Ir(ppy)$_3$ ($\Phi = 0.15$) are 4−5 times higher than their Schiff base-based analogues but lower than the quantum yield of *fac*-Ir(ppy)$_3$ ($\Phi = 0.40$). The solid-state emissions of PCZIr(ppy)$_3$ and PCZ(CH$_2$)$_4$Ir(ppy)$_3$ are exactly the same as the reference compound *fac*-Ir(ppy)$_3$ (Figure 4). However, both PSIr(ppy)$_3$ and PS(CH$_2$)$_4$Ir(ppy)$_3$ show a yellow emission in the solid state with maxima around 550 nm and a shoulder at 518 nm (Table 1). We suggest that the red shift in the solid state might be due to an aggregation-induced emission as has been observed before for Ir(III) complexes.[32] Lo et al.[32] observed that the solid-state luminescence of dendrimer-supported Ir(III) complexes exhibit a spectral red shift relative to its solution spectra.

The solution emission intensities and lifetimes of all *fac*-Ir(ppy)$_3$ functionalized polymers increased upon degassing of the solutions with nitrogen (Table 1). For instance, the luminescence lifetime of PSIr(ppy)$_3$ increased from 45 to 1221 ns after deaeration. Nevertheless, the spectral profiles were unchanged. This is indicative of quenching of the relatively long-lived ^{3}MLCT state by oxygen, presumably resulting in the formation of singlet oxygen. The luminescent lifetimes of the $-N{=}CH-$ containing polymers are shorter than their reducing counterparts, which is consistent with their lower luminescent quantum yields. As indicated in Table 1, the ratio of the emission quantum yield and lifetime (formally representing the product of the intersystem crossing yield and the radiative decay rate constant) varies by less than a factor of 3 for the series of complexes, suggesting the emission arises from the same state (^{3}MLCT) for all complexes. The copolymers containing carbazole have luminescence lifetimes that are comparable to their analogues lacking the carbazole; thus, there is no evidence for quenching of the Ir(III) complex ^{3}MLCT state by the carbazole, consistent with earlier observations.[46]

Time-Resolved Transient Difference Absorption Spectrum. Time-resolved transient difference absorption spectros-

Table 1. Photophysical Properties of Polymers[a]

no.	compound	solution emission[b] λ_{max}, (nm)	solid-state emission[c] λ_{max}, (nm)	Φ^c	τ (ns), air (deaerated)[e]	$\eta_{isc}k_r$, $\times 10^{-5}$ (s^{-1})
1	*fac*-Ir(ppy)$_3$	514	517	0.4[d]	29 (2000[c])	2.0
2	Ir(fppy)(ppy)$_2$	600	610	0.04	21 (478)	0.84
3	PSN=CHIr(ppy)$_3$	554	550	0.04	58 (287)	1.4
4	PSIr(ppy)$_3$	514	519,[f] 550	0.23	45 (1221)	1.9
5	PS(CH$_2$)$_4$N=CHIr(ppy)$_3$	548	550	0.03	50 (358)	0.84
6	PS(CH$_2$)$_4$Ir(ppy)$_3$	516	517,[f] 552	0.19	33 (1006)	1.9
7	PCZN=CHIr(ppy)$_3$	553	554	0.02	31 (292)	0.68
8	PCZ Ir(ppy)$_3$	517	517	0.12	33 (963)	1.2
9	PCZ(CH$_2$)$_4$N=CHIr(ppy)$_3$	551	558	0.05	61 (453)	1.1
10	PCZ(CH$_2$)$_4$Ir(ppy)$_3$	514	518	0.15	26 (1082)	1.4

[a] Luminescence measurements were carried out at $\lambda_{ex} = 380$ nm. [b] Aerated CH$_2$Cl$_2$ solution at room temperature. [c] Quartz slide at room temperature. [d] In deaerated CH$_2$Cl$_2$ solutions using *fac*-Ir(ppy)$_3$ ($\Phi = 0.40$, in toluene) as standard.[34,45] [e] Luminescent lifetime in THF solution. [f] Shoulder peak.

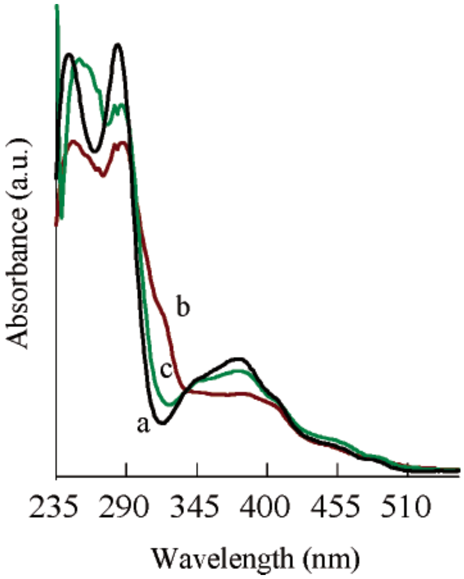


Figure 1. UV–vis absorption spectra in CH$_2$Cl$_2$: (a) *fac*-Ir(ppy)$_3$, (b) PS(CH$_2$)$_4$N=CHIr(ppy)$_3$, and (c) PS(CH$_2$)$_4$Ir(ppy)$_3$.

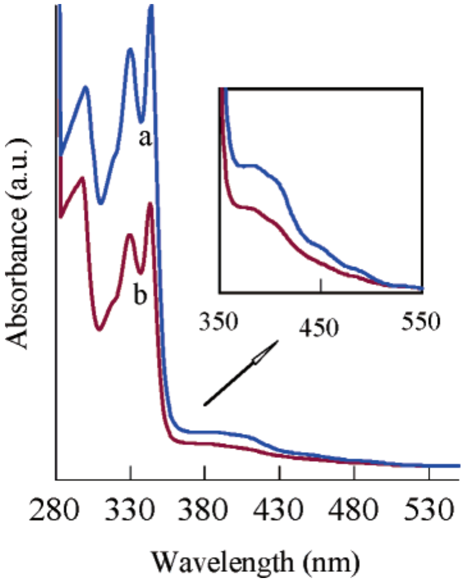


Figure 2. UV–vis absorption spectra in CH$_2$Cl$_2$: (a) PCZ(CH$_2$)$_4$N=CHIr(ppy)$_3$ and (b) PCZ(CH$_2$)$_4$Ir(ppy)$_3$.

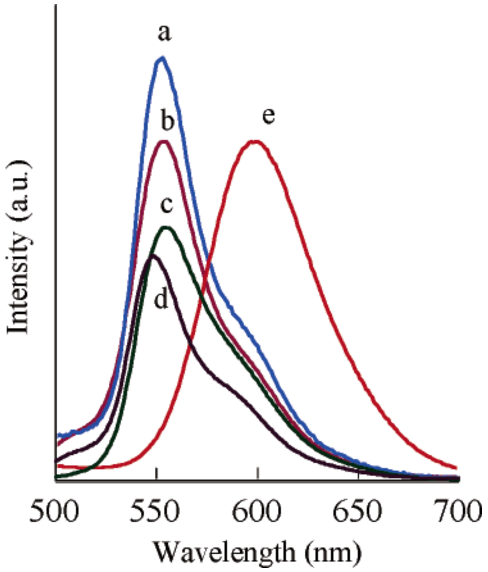


Figure 3. Photoluminescence emission spectra: solution in CH$_2$Cl$_2$ (curves a, c, e) and solid-state (curves b, d) emission spectra: (a, b) PCZ(CH$_2$)$_4$N=CHIr(ppy)$_3$, (c, d) PS(CH$_2$)$_4$N=CHIr(ppy)$_3$, and (e) *fac*-Ir(fppy)(ppy)$_2$ ($\lambda_{ex} = 380$ nm).

copy has rarely been employed to investigate cyclometalated Ir(III) complexes.[42−44] The transient absorption spectrum of the parent *fac*-Ir(ppy)$_3$ complex (Figure 5) shows an absorption band in the UV region with a maximum around 300 nm, bleaching of the ground-state absorption at 390 nm, and a weak excited-state absorption around 480 nm. The strong negative feature at 510 nm results from transient luminescence of the complex (TA spectra were not corrected for sample luminescence). Like *fac*-Ir(ppy)$_3$, *fac*-Ir(fppy)(ppy)$_2$ also has a bleaching associated with its steady-state emission at 590 nm (Figure 6), but its transient spectrum exhibits a strong absorption band extending from 320 nm to the visible region with two maxima at 380 and 430 nm. Furthermore, the spectra display a weak absorbance beyond 730 nm, and no ground-state bleaching was observed in the 300−450 nm region. The transient absorption spectra of *fac*-Ir(ppy)$_3$ functionalized polymers were found to be divided into two groups. The −N=CH− containing polymers and their reduced counterparts showed very similar transient absorption behavior to that of *fac*-Ir(fppy)(ppy)$_2$ and *fac*-Ir(ppy)$_3$, respectively. The transient absorption spectrum of PS(CH$_2$)$_4$N=CHIr(ppy)$_3$ has three features as shown in Figure 7. Strong absorption is observed extending from 320 to 500 nm with two maxima at 370 and 430 nm. Furthermore, there is also a bleaching corresponding to the steady-state emission at 550 nm. Finally, there is a strong specific absorption band in the red region with a maximum at 800 nm, which might be associated with the −N=CH−ppy moiety. The remarkable likeness of the transient spectra of PS(CH$_2$)$_4$N=CHIr(ppy)$_3$ and *fac*-Ir(fppy)(ppy)$_2$ suggests that the excited state of the polymer complex may be localized on the phenylpyridine ligand containing the unsaturated substituent. The transient absorption spectrum of the reduced

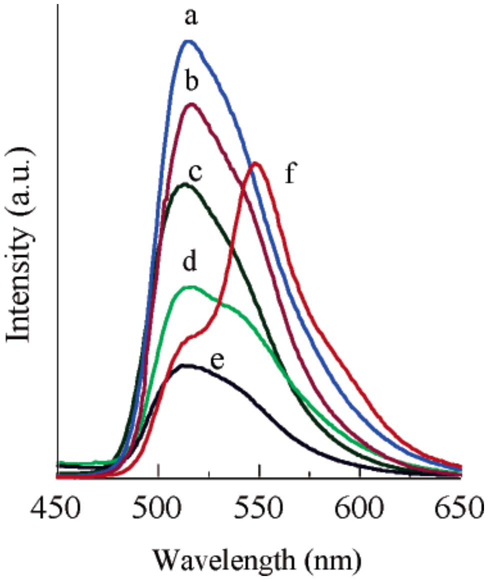


Figure 4. Photoluminescence emission spectra: solution in CH_2Cl_2 (curves a, c, e) and solid-state (curves b, d, f) emission spectra: (a, b) *fac*-Ir(ppy)$_3$, (c, d) PCZ(CH_2)$_4$Ir(ppy)$_3$, and (e, f) PS(CH_2)$_4$Ir(ppy)$_3$ (λ_{ex} = 380 nm).

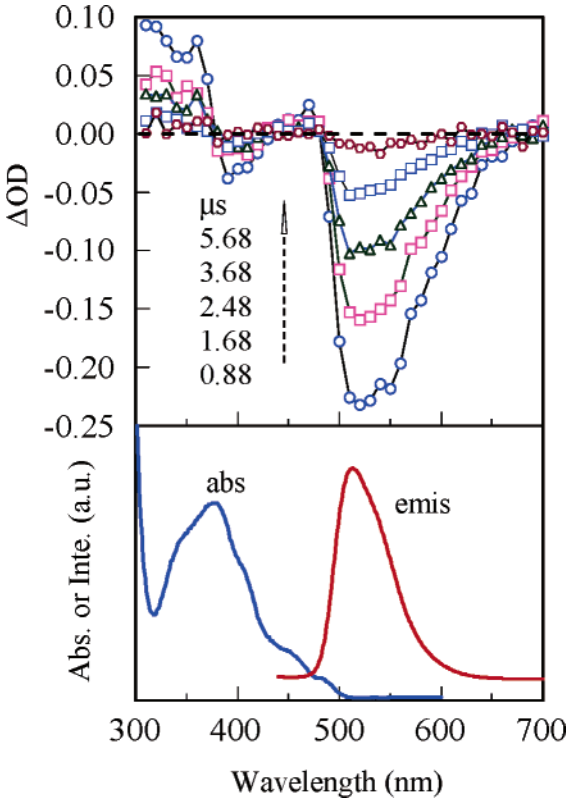


Figure 5. Time-resolved transient difference absorption spectrum (top, λ_{ex} = 420 nm); steady-state absorption and emission (bottom, λ_{ex} = 380 nm) of *fac*-Ir(ppy)$_3$ in THF.

polymer PS(CH_2)$_4$Ir(ppy)$_3$ (Figure 8) has two absorptions with maxima at 360 and 450 nm and two bleachings associated with the ground-state absorption at 390 nm and the other corresponds to the steady-state emission. The absorption features differ from those of Ir(ppy)$_3$ and suggest that, while the emission maxima and luminescence lifetimes of the two complexes are similar, subtle differences in the excited-state electronic structure exist between the parent complex and the polymer appended complex. In all cases, the lifetimes measured by transient absorption for both aerated and degassed samples differed by less than 10% from the values obtained using time-resolved emission, indicating that the excited state observed is the same in both characterization methods and that the emission observed is in no case resulting from an impurity in solution.

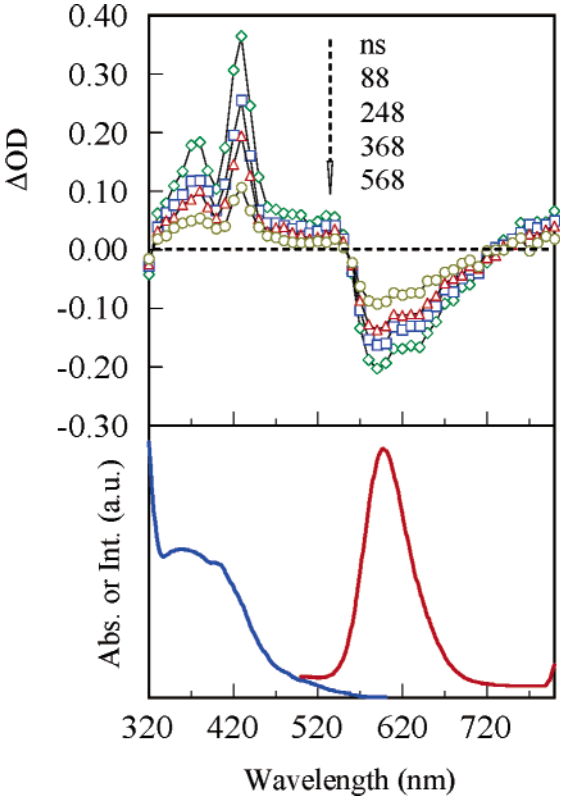


Figure 6. Time-resolved transient difference absorption spectrum (top, λ_{ex} = 420 nm); steady-state absorption and emission (bottom, λ_{ex} = 380 nm) of *fac*-Ir(fppy)(ppy)$_2$ in THF.

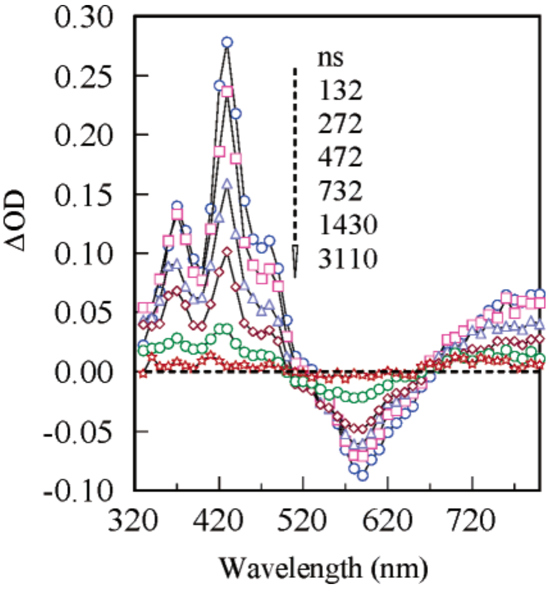


Figure 7. Time-resolved transient difference absorption spectrum of PS(CH_2)$_4$N=CHIr(ppy)$_3$ in THF (λ_{ex} = 420 nm).

Conclusions and Summary

We have developed an efficient synthetic approach for the synthesis of *fac*-Ir(ppy)$_3$ complex functionalized poly(styrene)s and poly(9-vinylcarbazole)-*co*-poly(styrene)s. The emission wavelength of all polymers could be readily tuned from 550 to

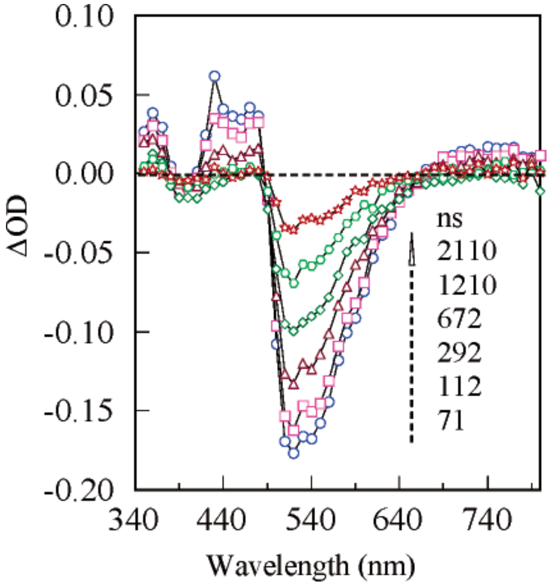


Figure 8. Time-resolved transient difference absorption spectrum of PS$(CH_2)_4$Ir(ppy)$_3$ in THF (λ_{ex} = 420 nm).

515 nm by reducing the Schiff base linkage of the Ir(III) complex to an amine. The reduced polymers have photophysical properties (high quantum yields and long luminescent lifetimes) similar to those of the corresponding small molecule *fac*-Ir(ppy)$_3$ although transient absorption spectra exhibit distinct differences that suggest that the localization of the excited state differs from the parent complex. These results clearly demonstrate that *fac*-Ir(ppy)$_3$ complex functionalized poly(styrene)s and poly(9-vinylcarbazole)-*co*-poly(styrene)s are potentially outstanding emissive materials for polymeric OLED devices.

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