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ORIGINAL ARTICLE

Synthesis of *fac*-Ir(ppy)$_3$ end-functionalized poly(4-diphenylaminostyrene) using *fac*-Ir(ppy)$_2$(vppy) as a single-monomer addition reagent

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The compound *fac*-Ir(ppy)$_3$ (*fac*, facial; ppy, 2-phenylpyridyl) end-functionalized poly(4-diphenylaminostyrene) (PDAS) was synthesized by adding *fac*-Ir(ppy)$_2$(vppy) (vppy,2-(4-vinylphenyl)pyridyl) to poly(4-diphenylaminostyryl)lithium (PDASLi). In this reaction, *fac*-Ir(ppy)$_2$(vppy) acts as a *fac*-Ir(ppy)$_3$ single-monomer addition reagent for PDASLi. The first *fac*-Ir(ppy)$_2$(vppy) molecule readily binds to the carbanion of PDASLi, but the addition of a second *fac*-Ir(ppy)$_2$(vppy) molecule to the carbanion on the vinyl group of *fac*-Ir(ppy)$_2$(vppy) does not proceed. Thus, *fac*-Ir(ppy)$_3$ end-functionalized PDAS, which consists of one PDAS molecule and one *fac*-Ir(ppy)$_3$ molecule, was successfully obtained for the first time.

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INTRODUCTION

Among various semi-conducting polymers, poly(4-diphenylaminostyrene) (PDAS), a stable and soluble triphenylamine-containing polymer, has been recognized as an attractive hole-transport polymer for optoelectronic applications.[1–19] To obtain PDAS with a well-defined and well-controlled polymer chain structure, different anionic,[1,3] radical and living radical[1,2,4–11] methods have been performed using 4-diphenylaminostyrene (4-DAS), the monomer of PDAS. However, the controlled polymerization of 4-DAS is considerably difficult, even with living radical polymerization.

To obtain PDAS with a well-defined polymer chain structure,[12–19] we discovered the first successful living anionic polymerization of 4-DAS.[12] Subsequently, the stereoregularity and the properties of PDAS were revealed,[12,14] and the living anionic polymerization of 4-DAS was expected to help producing various end-functionalized PDAS.[13,18] Among them, the semi-conducting polymer *fac*-Ir(ppy)$_3$ (*fac*, facial; ppy, 2-phenylpyridyl) end-functionalized PDAS has been a good candidate for organic light-emitting diodes (OLEDs) because PDAS has good solubility[14] and *fac*-Ir(ppy)$_3$ is an outstanding phosphorescent material. If this end-functionalized PDAS is successfully obtained, a homogeneous dispersion of *fac*-Ir(ppy)$_3$ for effective triplet energy transfer seems achievable.

We have previously demonstrated[20] that *fac*-Ir(ppy)$_2$(vppy) (vppy = 2-(4-vinylphenyl)pyridyl) can act as a single-monomer addition reagent for poly(1,3-cyclohexadienyl)lithium (PCHDLi, a living polymer of poly(1,3-cyclohexadiene)) to produce *fac*-Ir(ppy)$_3$ end-functionalized poly(1,3-cyclohexadiene) (Scheme 1, living polymer = PCHDLi). The results indicated that this reaction was an effective method to obtain various *fac*-Ir(ppy)$_3$ end-functionalized polymers with well-controlled and defined polymer chain structures.

In our previous publication,[13] we demonstrated that the PDAS carbanion has a lower nucleophilicity than the poly(1,3-cyclohexadiene) carbanion. In other words, *fac*-Ir(ppy)$_2$(vppy) was considerably more difficult to add to poly(4-diphenylaminostyryl)lithium (PDASLi, a living polymer of PDAS) than to PCHDLi. Therefore, it was important to examine the possibility of *fac*-Ir(ppy)$_2$(vppy) as a *fac*-Ir(ppy)$_3$ single-monomer addition reagent for PDASLi. There upon, we attempted to add *fac*-Ir(ppy)$_2$(vppy) to PDASLi to synthesize *fac*-Ir(ppy)$_3$ end-functionalized PDAS.

Herein, we report the first successful synthesis of *fac*-Ir(ppy)$_3$ end-functionalized PDAS. The characteristics of the *fac*-Ir(ppy)$_2$ (vppy)-to-PDASLi addition reaction are also discussed in detail.

EXPERIMENTAL PROCEDURE

Materials

Toluene (⩾99.8%) was refluxed over calcium hydride (CaH_2, 95%) and then distilled under dry argon. Methyltriphosphonium bromide (⩾98.0%) and 4-(2-pyridyl)benzaldehyde (⩾95.0%) were dried under reduced pressure. The compound 4-DAS[12] and 2-(4-vinylphenyl)pyridine[20] were prepared via the previously reported standard Wittig reactions. Tetrakis(2-phenylpyridine-C^2,N')(μ-dichloro)diiridium $(Ir(ppy)_2Cl)_2$ was prepared according to a procedure described in the literature,[21] and *fac*-Ir(ppy)$_2$(vppy) was prepared

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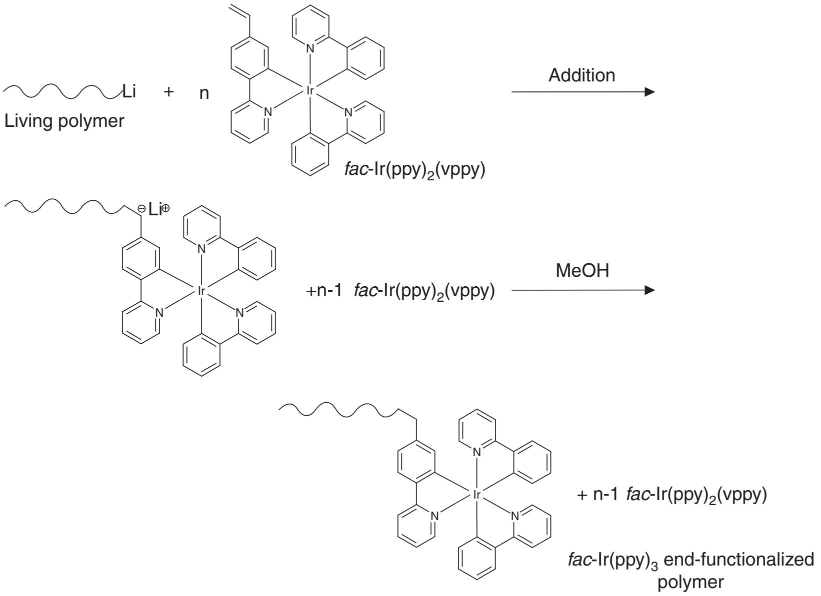


Scheme 1 Addition reaction between living polymer (polymer lithium) and *fac*-Ir(ppy)$_2$(vppy).

according to our previously reported procedure.[20] Other reagents were used as received, unless stated otherwise. Methyltriphosphonium bromide, 4-(2-pyridyl)benzaldehyde and 2-phenylpyridine (⩾98.0%) were purchased from Tokyo Chemical (Tokyo, Japan). Iridium(III) chloride trihydrate ($IrCl_3 \cdot 3H_2O$, ⩾90.0%) was purchased from Kanto Chemical (Tokyo, Japan). All other reagents were purchased from Sigma-Aldrich (St Louis, MO, USA).

Preparation of PDASLi

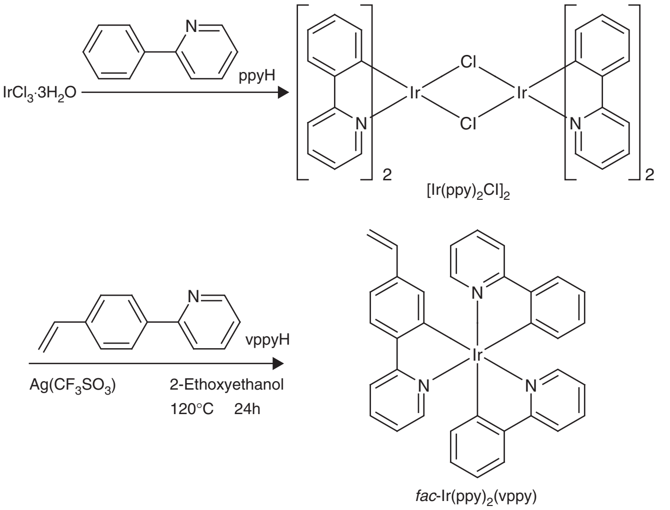
All substances were added into the container using a syringe. The compound 4-DAS (0.50 g, 1.85 mmol) was placed in a completely dry 50 ml Schlenk tube and dried under reduced pressure. The Schlenk tube was alternatively evacuated and filled with dry argon several times, after which 10.0 ml of toluene was added at room temperature (*ca.* 25 °C). Then, *t*-buyllithium (*t*-BuLi; 1.70 mol l^{-1} in pentane, 0.120 or 0.170 mmol) was injected into this solution, and the reaction mixture was magnetically stirred under dry argon at room temperature for 3 h, producing PDASLi in *ca.* 70 wt% yield. (Note: Although the best initiator for the anionic polymerization of 4-DAS was the benzyllithium/*N,N,N′,N′*-tetramethylethylenediamine system,[12] in this study, *t*-BuLi was used as an initiator in order to simplify the analysis of proton nuclear magnetic resonance (^{1}H NMR) spectrum of *fac*-Ir(ppy)$_3$ end-functionalized PDAS.)

Addition of *fac*-Ir(ppy)$_2$(vppy) to PDASLi

A completely dry 150 ml Schlenk tube was purged with dry argon, and *fac*-Ir(ppy)$_2$(vppy) (0.25 wt% solution in toluene) was added at room temperature (*ca.* 25 °C) using a syringe. A toluene solution of PDASLi was then injected to this Schlenk tube, and the reaction mixture was magnetically stirred under dry argon at room temperature for 96 h. Afterward, to terminate the addition reaction, dry methanol (MeOH, ⩾99.8%) was added to the reaction mixture in an equimolar amount to the amount of Li atoms present in the mixture. Then, the reaction mixture was poured into a large volume of ethanol (EtOH) to precipitate the polymer, which was separated by filtration. The product was washed with excess EtOH and dried under reduced pressure at room temperature for 24 h, resulting in a powdery orange polymer.

Measurements

The number of average molecular weight (M_n), the weight of average molecular weight (M_w) and the polydispersity index (M_w/M_n) were determined using a gel permeation chromatography equipment with a differential refractive index detector (Shimadzu RID-6A (Shimadzu, Kyoto, Japan)), a ultraviolet detector (Shimadzu SPD-6 A) and a Shimadzu Shim-pack GPC-80M column (length: 300 mm, diameter: 8 mm, effective molecular weight range of 100–4 000 000) at 40 °C. Tetrahydrofuran (THF) was used as the eluent, and the flow rate was 1.00 ml min^{-1}. A molecular weight calibration curve was obtained using the polystyrene standards. The ^{1}H NMR spectra were measured in deuterated chloroform or THF (THF-d_8) at 500 MHz using a Jeol ECA 500 spectrometer (Jeol, Tokyo, Japan).



Scheme 2 Synthesis of *fac*-Ir(ppy)$_2$(vppy).

RESULTS AND DISCUSSION

Synthesis of *fac*-Ir(ppy)$_2$(vppy)

According to our previously reported procedure (Scheme 2),[20] the synthesis of *fac*-Ir(ppy)$_2$(vppy) was performed at 120 °C in 2-ethoxyethanol for 24 h. The obtained result is the thermodynamically favored *fac*-isomer (that is, *fac*-Ir(ppy)$_2$(vppy), an orange powdery compound) with relatively high yield (*ca.* 48%). The complex was soluble in THF and partially soluble in EtOH, chloroform, dichloromethane and toluene.

Figure 1 shows a typical ^{1}H NMR spectrum of *fac*-Ir(ppy)$_2$(vppy). The peaks from 6.6 to 7.9 p.p.m. ($H_a = 3H$, $H_{b,c,d} = 9H$ and $H_{e,f,g} = 11H$) and from 4.8 to 6.5 p.p.m. ($H_o = 1H$, $H_p = 1H$ and $H_q = 1H$) were assigned to aromatic and olefinic protons, respectively, as previously reported.[22] The complexation of the Ir(III) ion led to a general diamagnetic shift of the ^{1}H NMR signals of *fac*-Ir(ppy)$_2$(vppy).

Synthesis of *fac*-Ir(ppy)$_3$ end-functionalized PDAS

We have previously reported[14] that PDAS is an excellent semiconducting polymer, and *fac*-Ir(ppy)$_3$ is an outstanding phosphorescent material. Thus, it was expected that *fac*-Ir(ppy)$_3$ end-functionalized PDAS would be a suitable material for OLEDs. To obtain *fac*-Ir(ppy)$_3$ end-functionalized PDAS, *fac*-Ir(ppy)$_2$(vppy) was added to PDASLi under various reaction conditions. The result showed that this addition reaction was unstable: the addition of polar additives, such as ethers (or amines), caused *fac*-Ir(ppy)$_2$(vppy) to decompose, and a high reaction temperature deactivated PDASLi. From the results obtained, the optimized reaction condition was found.

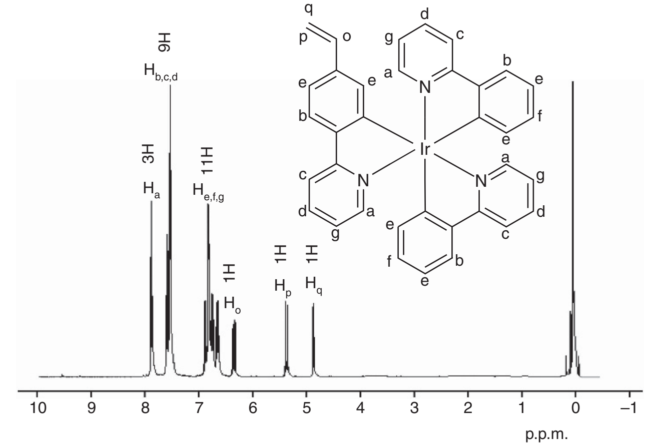


Figure 1 ^{1}H NMR spectrum of *fac*-Ir(ppy)$_2$(vppy), measured as a 3.0 wt% solution in THF-d_8 at 50 °C.

Scheme 3 illustrates that *fac*-Ir(ppy)$_2$(vppy) was added to PDASLi ($[\text{4-DAS}]_0/[t\text{-BuLi}]_0 = 15.4$) (Note: Although the best initiator for the anionic polymerization of 4-DAS was the benzyllithium/*N,N,N′,N′*-tetramethylethylenediamine system,[12] in this study, *t*-BuLi was used as an initiator in order to simplify the analysis of ^{1}H NMR spectrum of *fac*-Ir(ppy)$_3$ end-functionalized PDAS) under dry argon in toluene at room temperature for 96 h ($[\textit{fac}\text{-Ir(ppy)}_2\text{(vppy)}]_0/[\text{PDASLi}]_0$ molar ratio = 1.20/1.00); the reaction produces an orange product in almost quantitative yield.

Figure 2 shows the gel permeation chromatography traces of the original PDAS (Figure 2a) and the reaction product (Figure 2b). The M_n value of the reaction product (5800 g mol^{-1}, polydispersity index = 1.24) was greater than that of the original PDAS ($M_n = 4590$ g mol^{-1}, polydispersity index = 1.27), which suggests that *fac*-Ir(ppy)$_2$(vppy) was successfully added to PDASLi.

Typical ^{1}H NMR spectra of the original PDAS and the reaction product are shown in Figure 3. For the original PDAS (Figure 3a), the peaks from 6.4 to 7.3 p.p.m. were assigned to the aromatic protons (H_v) in the 4-DAS units. The peaks from 1.2 to 2.5 p.p.m. were assigned to the methine and methylene protons (H_w) in the

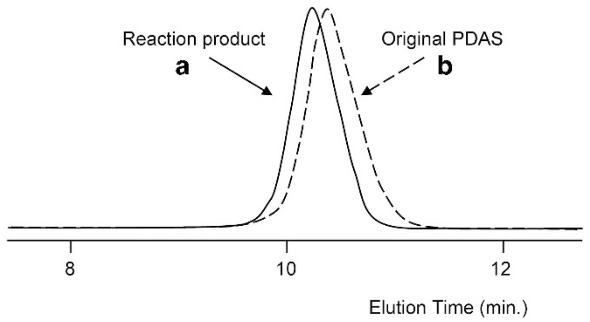
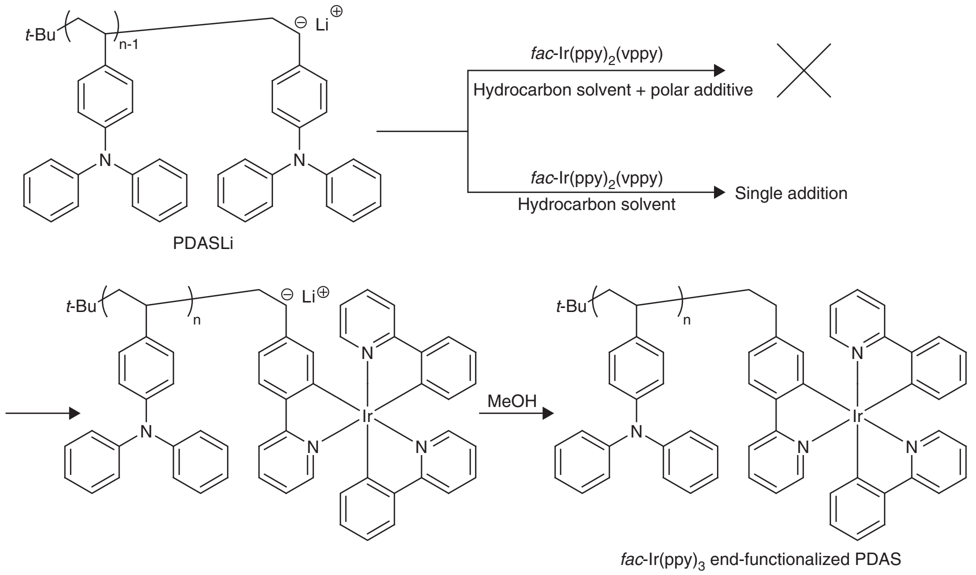


Figure 2 Gel permeation chromatography traces of (**a**) the original PDAS ($M_n = 4590$ g mol^{-1}, polydispersity index (PDI) = 1.27) and (**b**) the reaction product ($M_n = 5800$ g mol^{-1}, PDI = 1.24).



Scheme 3 Addition reaction between PDASLi and *fac*-Ir(ppy)$_2$(vppy).

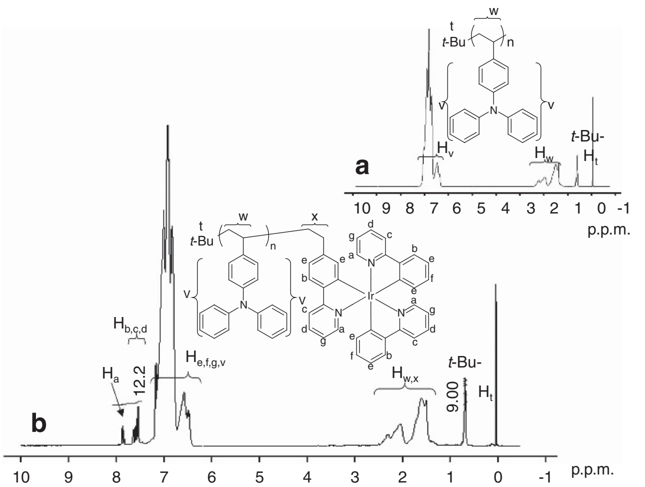


Figure 3 ^{1}H NMR spectra of (**a**) PDAS ($M_n = 4590\,g\,mol^{-1}$, PDI = 1.27) and (**b**) *fac*-Ir(ppy)$_3$ end-functionalized PDAS ($M_n = 5800\,g\,mol^{-1}$, PDI = 1.24), measured as a 3.0 wt% solution in deuterated chloroform at 50 °C.

4-DAS units. The peaks approximately 0.9 p.p.m. were assigned to the methyl protons (H_t) in the *t*-butyl residues from *t*-BuLi.[12,14] For the reaction product (Figure 3b), new peaks appeared approximately 7.6 and 7.8 p.p.m., which were assigned to the aromatic protons ($H_{a–d}$) in the *fac*-Ir(ppy)$_3$ end-functional groups.[20] Therefore, it was confirmed that the reaction product was *fac*-Ir(ppy)$_3$ end-functionalized PDAS.

In the anionic polymerization of 4-DAS, each molecule of *t*-BuLi produces one molecule of PDASLi.[12] The fractional yield of *fac*-Ir(ppy)$_3$ end-functionalized PDAS (that is, (*fac*-Ir(ppy)$_3$ end-functionalized PDAS)/(*fac*-Ir(ppy)$_3$ end-functionalized PDAS) + (free PDAS)) could be estimated by comparing the peak areas of the $H_{a–d}$ and H_t peaks (1.0 mol $H_{a–d} = 12H$, 1.0 mol $H_t = 9H$). From the ^{1}H NMR spectrum of the reaction product (Figure 3b), the fractional yield of *fac*-Ir(ppy)$_3$ end-functionalized PDAS was calculated to be 100% (12.2/12 = 1.02). Therefore, *fac*-Ir(ppy)$_3$ end-functionalized PDAS with a well-controlled and defined polymer chain structure was successfully obtained for the first time, and *fac*-Ir(ppy)$_2$(vppy) appeared to act as a *fac*-Ir(ppy)$_3$ single-monomer addition reagent for PDASLi, as in the case of *fac*-Ir(ppy)$_3$ end-functionalized poly(1,3-cyclohexadiene).[20] The obtained *fac*-Ir(ppy)$_3$ end-functionalized PDAS is soluble in common organic solvents, such as THF, chloroform, dichloromethane, toluene and *N*,*N*-dimethylformamide.

To confirm that *fac*-Ir(ppy)$_2$(vppy) is a *fac*-Ir(ppy)$_3$ single-monomer addition reagent for PDASLi, we performed the anionic polymerization of 4-DAS with *t*-BuLi in toluene (Note: Although the best initiator for the anionic polymerization of 4-DAS was the benzyllithium/*N*,*N*,*N′*,*N′*-tetramethylethylenediamine system,[12] in this study, *t*-BuLi was used as an initiator in order to simplify the analysis of ^{1}H NMR spectrum of *fac*-Ir(ppy)$_3$ end-functionalized PDAS) and the subsequent addition of *fac*-Ir(ppy)$_2$(vppy) to PDASLi in toluene ([*fac*-Ir(ppy)$_2$(vppy)]$_0$/[PDASLi]$_0$ molar ratio = 1.00/1.00, 2.00/1.00 and 3.00/1.00) were attempted, as shown in Scheme 1 (living polymer = PDASLi, *n* = 1–3). The results obtained are summarized in Table 1.

Table 1 Single-monomer addition reaction between *fac*-Ir(ppy)$_2$(vppy) and PDASLi

	Polymerization[a]			*Addition reaction*[b]			
		PDAS prepolymer			*fac-Ir(ppy)$_3$ end-functionalized PDAS*		
Number	*[4-DAS]$_0$/ [t-BuLi]$_0$ (molar ratio)*	M$_n$ *(g mol^{-1})*	*PDI*	*[fac-Ir(ppy)$_2$(vppy)]$_0$/ [PDASLi]$_0$ (molar ratio)*	M$_n$ *(g mol^{-1})*	*PDI*	*fac-Ir(ppy)$_3$/ PDAS*[c]
1	10.9/ 1.00	3390	1.27	1.00/1.00	4810	1.24	1/1
2	10.9/ 1.00	3140	1.29	2.00/1.00	4660	1.26	1/1
3	10.9/ 1.00	3250	1.28	3.00/1.00	4700	1.23	1/1

Abbreviations: DAS, diphenylaminostyrene; *fac*, facial; PDAS, poly(4-diphenylaminostyrene); PDI, polydispersity index; ppy, 2-phenylpyridyl.
[a] The polymerization of 4-DAS was carried out in toluene under dry argon at room temperature for 3 h.
[b] The addition of *fac*-Ir(ppy)$_2$(vppy) to PDASLi was carried out in toluene under dry argon at room temperature for 96 h.
[c] Estimated by ^{1}H NMR.

After the addition reaction, the M_n value of each obtained polymer was considerably higher than that of the original PDAS, which produces *fac*-Ir(ppy)$_3$ end-functionalized PDAS. However, the M_n values of all *fac*-Ir(ppy)$_3$ end-functionalized PDAS were almost the same, although the molar ratios of [*fac*-Ir(ppy)$_2$(vppy)]$_0$/[PDASLi]$_0$ were 1.00/1.00, 2.00/1.00 and 3.00/1.00. This result reveals that in the addition reaction, only one *fac*-Ir(ppy)$_2$(vppy) molecule can bind to the carbanion of PDASLi, as shown in Scheme 1. The addition of a second *fac*-Ir(ppy)$_2$(vppy) molecule to the carbanion on the vinyl group of *fac*-Ir(ppy)$_2$(vppy) is difficult because of the low nucleophilicity and the large steric hindrance of the carbanion. To confirm this hypothesis, the functionality of these polymers was examined using ^{1}H NMR spectroscopy. As expected, the ^{1}H NMR spectra of all polymers obtained were similar to that shown in Figure 3b. The integrated ratio of $H_{a–d}/H_t$ protons for all *fac*-Ir(ppy)$_3$ end-functionalized PDAS was close to the theoretical value (12/9), as shown in Figure 3b. Therefore, all obtained polymers consisted of one *fac*-Ir(ppy)$_3$ molecule and one PDAS molecule (Scheme 3).

The results of the addition reaction between *fac*-Ir(ppy)$_2$(vppy) and PDASLi confirm that homopolymerization of *fac*-Ir(ppy)$_2$(vppy) does not occur; instead, only one *fac*-Ir(ppy)$_2$(vppy) molecule reacts with the carbanion of PDASLi and is selectively incorporated into the polymer chain end of PDAS (Scheme 3), similar to the case of PCHDLi.[20] Therefore, it is concluded that *fac*-Ir(ppy)$_2$(vppy) is an excellent *fac*-Ir(ppy)$_3$ single-monomer addition reagent for PDASLi to successfully obtain *fac*-Ir(ppy)$_3$ end-functionalized PDAS with a well-controlled and well-defined polymer chain structure.

CONCLUSION

The polymer *fac*-Ir(ppy)$_3$ end-functionalized PDAS was synthesized by adding *fac*-Ir(ppy)$_2$(vppy) to PDASLi. In this reaction, *fac*-Ir(ppy)$_2$(vppy) acts as a *fac*-Ir(ppy)$_3$ single-monomer addition reagent for PDASLi. The first *fac*-Ir(ppy)$_2$(vppy) molecule readily binds to the carbanion of PDASLi. However, a second *fac*-Ir(ppy)$_2$(vppy) molecule does not bind to the carbanion on the vinyl group of *fac*-Ir(ppy)$_2$(vppy) because of the low nucleophilicity and the large steric hindrance of this carbanion. Therefore, only one *fac*-Ir(ppy)$_2$(vppy) molecule is selectively incorporated into the polymer chain end of PDAS to produce *fac*-Ir(ppy)$_3$ end-functionalized PDAS, which consists of one PDAS molecule and one *fac*-Ir(ppy)$_3$ molecule. The obtained *fac*-Ir(ppy)$_3$ end-functionalized PDAS is soluble in common organic solvents, such as THF, chloroform, dichloromethane, toluene and *N*,*N*-dimethylformamide.

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