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Synthesis, and Photo- and Electro-Luminescent Properties of Phosphorescent Iridium- and Platinum-Containing Polymers

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1. Introduction

Development of polymer light-emitting diode (PLED) has been attracted considerable attentions,¹ because polymeric materials could be applied to low-cost production of electro-luminescent (EL) devices exhibiting efficient luminescence for flat-panel displays. As polymeric property of the materials enables the solution processes, such as spin-coating, screen printing, and ink-jet printing (Figure 1), large-area and fine-pixel displays could be easily developed in comparison with the vapor deposition process. In addition to such easy preparation, it is of significant that it requires a fewer number of layers in PLED devices, which enables low driving voltage, even though PLED still has a drawback in lower luminescence efficiency than that of the organic light-emitting diode (OLED) in general.

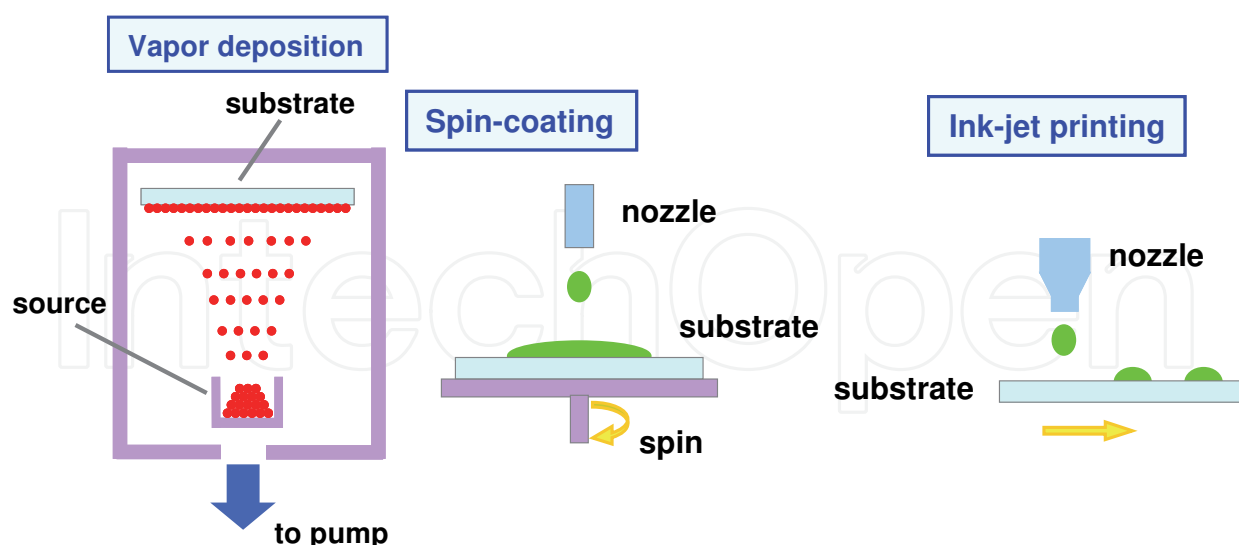


Fig. 1. Vapor deposition process, spin-coating, and ink-jet printing

In contrast to widely developed fluorescent π -conjugated polymers, such as polyfluorenes and polyphenylene vinylenes (PPVs), as polymeric EL materials (Figure 2),² researches for phosphorescent polymers are still now in progress, because it follows the development of the phosphorescent metal complexes, which are also in progress. Two types of

phosphorescent PLED materials are known: (1) host polymers such as poly(vinylcarbazole) (PVK) and poly(9,9-di-*n*-octyl-2,7-fluorene) (PFO), into which phosphorescent small molecules are doped,^{1a-f} and (2) polymers having phosphorescent pendant units in the side chain. In the former polymer, phase separation and crystallization of the small molecules in the polymer matrix may reduce the luminescence efficiency due to self-quenching mechanism and prevent uniform emission all over the films. Thus, several studies were focused on the latter phosphorescent polymer. Lee et al.³ and Tokito et al.⁴ independently developed non-conjugative copolymers in which monomers having luminescent cyclometalated iridium pendant units copolymerized (Figure 3), whereas Chen et al. reported preparation of a conjugative fluorene copolymer from a cyclometalated iridium-suspended co-monomer (Figure 4).⁵

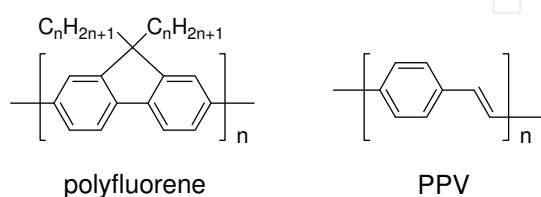


Fig. 2. Structure of polyfluorene and PPV

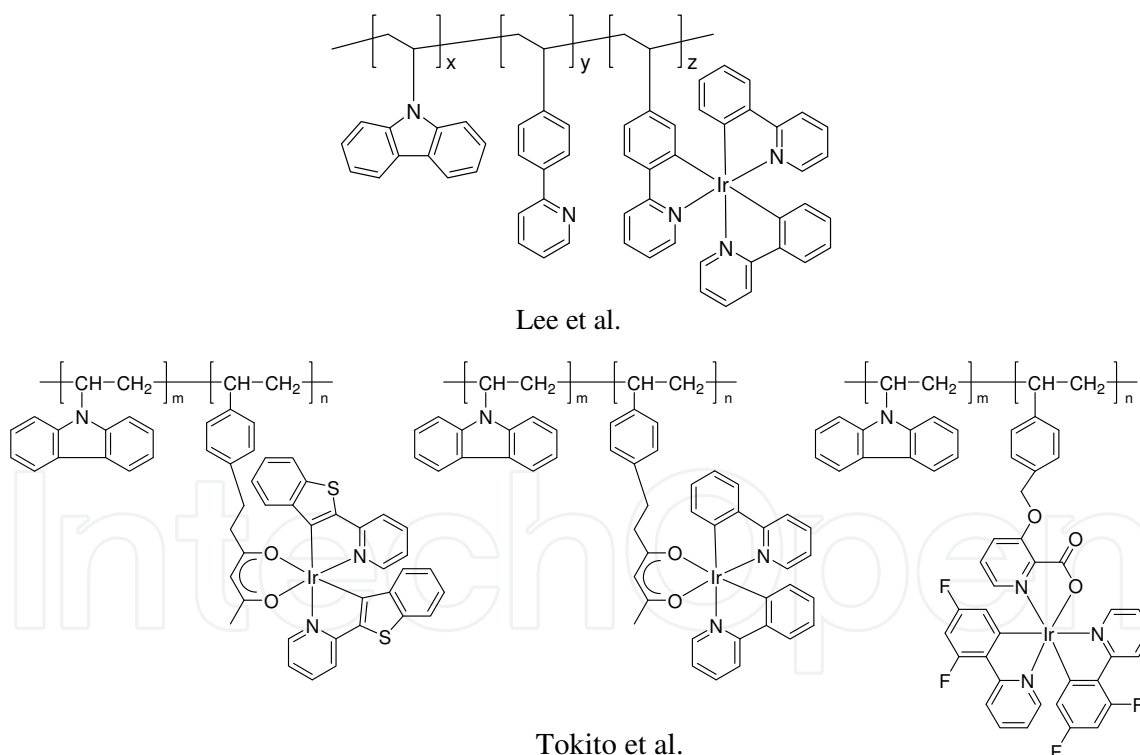


Fig. 3. Structure of non-conjugated copolymers with luminescent cyclometalated iridium pendant units

Scheme 1 depicts the general synthetic methodologies for the metallopolymer including the metal complex side chain. Almost all of the luminescent metallopolymer ((D) in Scheme 1) have been synthesized via monomers containing metal-complex pendant units (B) (Scheme 1, *Method A*).⁶ However, polymerization of these metal-containing monomers led to the

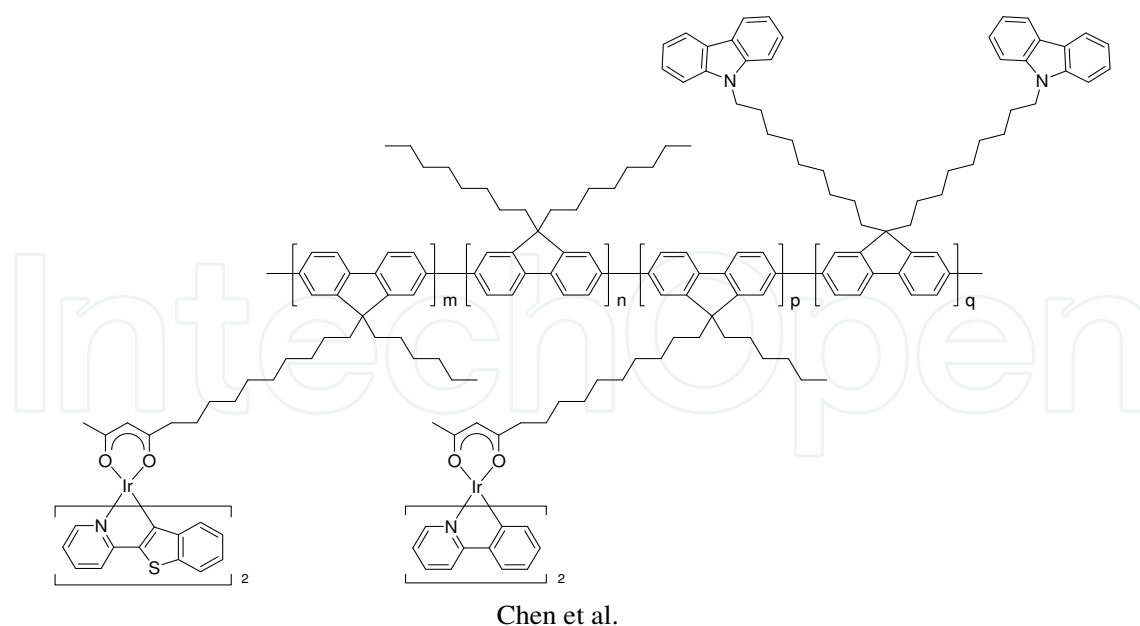
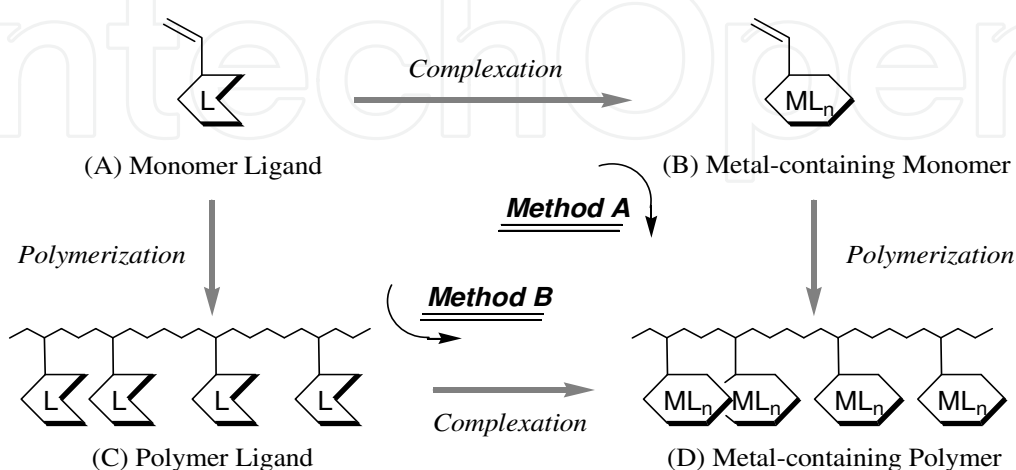


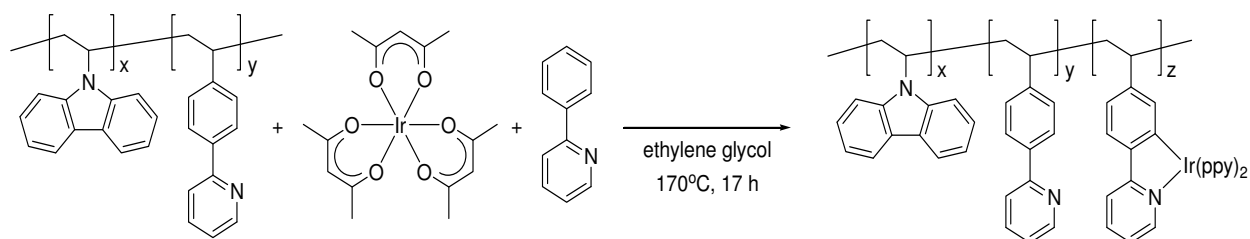
Fig. 4. Structure of conjugated fluorene copolymer with luminescent cyclometallated iridium pendant units

elimination of metal fragments to some extent or failure of polymer weight control. Alternatively, the polymer (D) can be synthesized by polymerization of a ligand-containing monomer followed by the reaction of the copolymer ligand (C) with a metal pendant unit (Scheme 1, *Method B*). *Method B* is seemed to be favored against *Method A* in the preparation of phosphorescent metallopolymer, because various kinds of ligand monomers can be easily copolymerized in desirable content with previously developed radical copolymerization processes in metal-containing polymer chemistry.⁷ However, in the early reports, synthesis of luminescent metallopolymer via *Method B* was conducted only under severe conditions, such as Lee, Schulz or Fréchet reported (Scheme 2, 3, 4).^{3,7g}

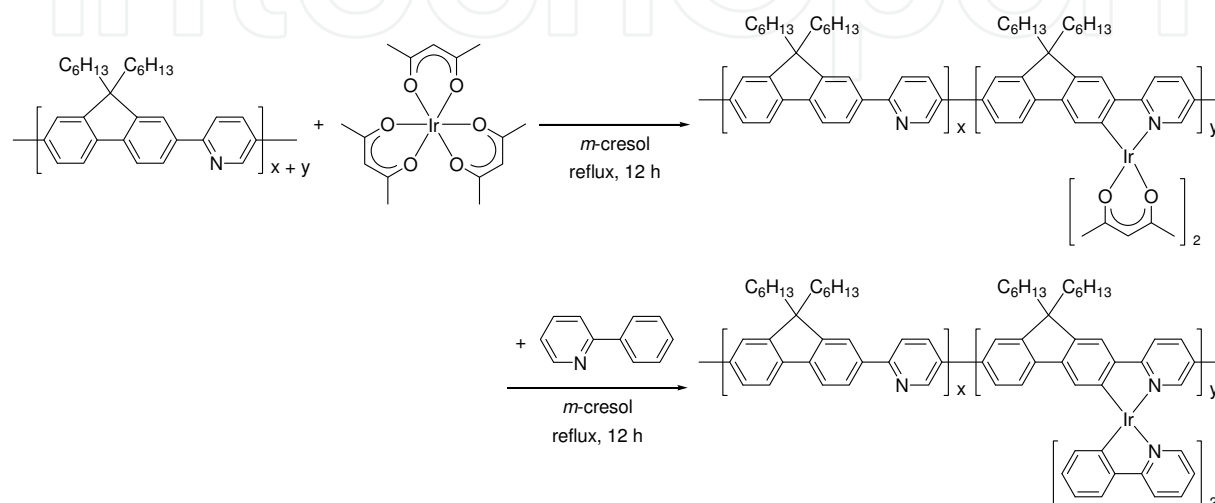
Furthermore, there are few examples that the alpha and/or omega ends of the polymers are capped with phosphorescent units for EL materials that can be provided by the final combination of the ligand unit units in the polymer ends with metal precursors.



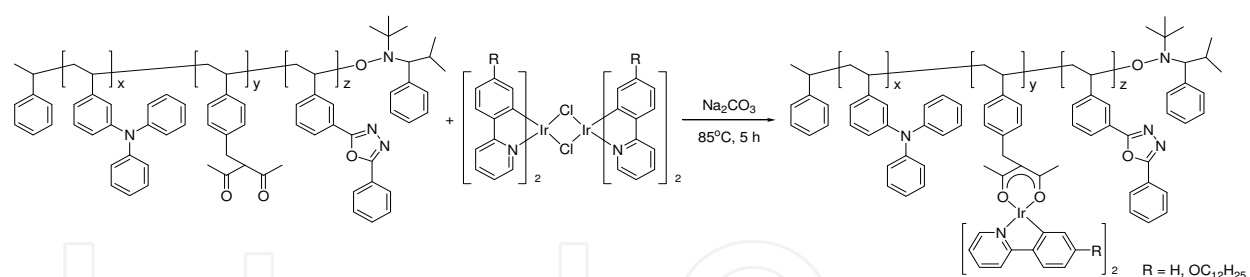
Scheme 1. Synthetic methodology of metal-containing polymer.



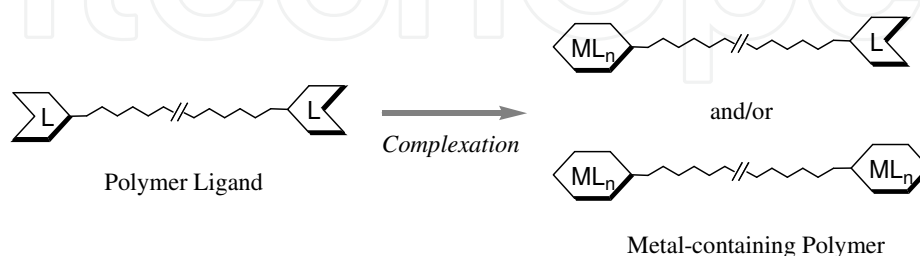
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

We previously developed metallopolymer produced from methyl methacrylate (MMA) and 4-styryldiphenylphosphine copolymers with an iridium precursor. The iridium polymers performed both photo- and electroluminescence, and showed characteristic

features depending upon the content ratios of the iridium and phosphorus in the copolymers.⁸ However, the devices containing these polymers exhibited rather low luminescent efficiency, because of its low charge-transporting ability caused by the nonconductive polyolefin backbone.

Here, we developed several series of iridium or platinum-containing metallopolymers under mild conditions in *Method B*, where pyridine was used as a linker module between the polymer main chain and the luminescent metal unit. Metal-incorporation effects of the metallopolymers on their luminescent properties were investigated in order to develop devices with high luminescent efficiency. Two independent types of the metallopolymers are shown in the following chapters: one is that composed of polyolefin main chain and metal units in its side chain, and the other is π -conjugated polymers, which has the luminescent metal groups in the chain ends.

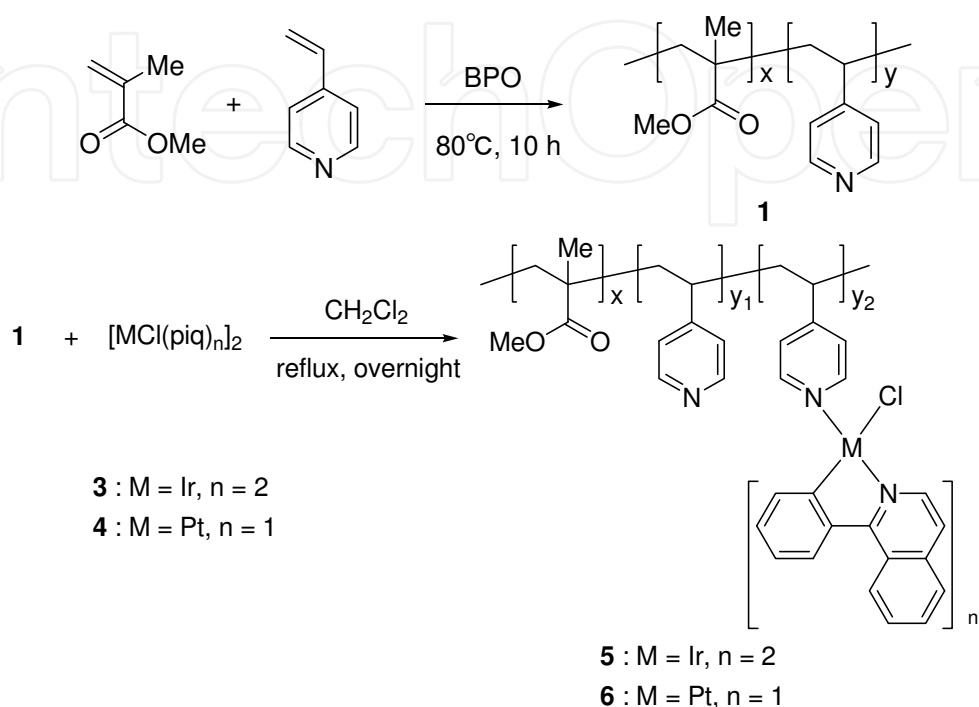
2. Preparation of metallopolymers containing polyolefin main chain

In the previous paper, we have reported that luminescent polymers can be easily prepared by the reaction of the phosphorus ligand copolymers derived from MMA and 4-styryldiphenylphosphine with the iridium precursor under mild conditions.⁸ Unfortunately, we found that the phosphorus side chain was easily oxidized to form oxide, probably leading to desorption of metal species from the metallopolymer. Alternatively, to improve the luminescent polymers, we used 4-vinylpyridine (Vp) as a linker module comonomer. It has been generally used as a ligand in metallopolymers.⁹ In this chapter, we have reported preparation of a series of new luminescent metallopolymers. First, pyridine-containing polymers were produced as ligands for metal modules. Then, some amount of iridium complex precursor, $[\text{IrCl}(\text{piq})_2]_2$ (**3**), where piqu is 1-phenylisoquinoline, was added to the ligand polymer.

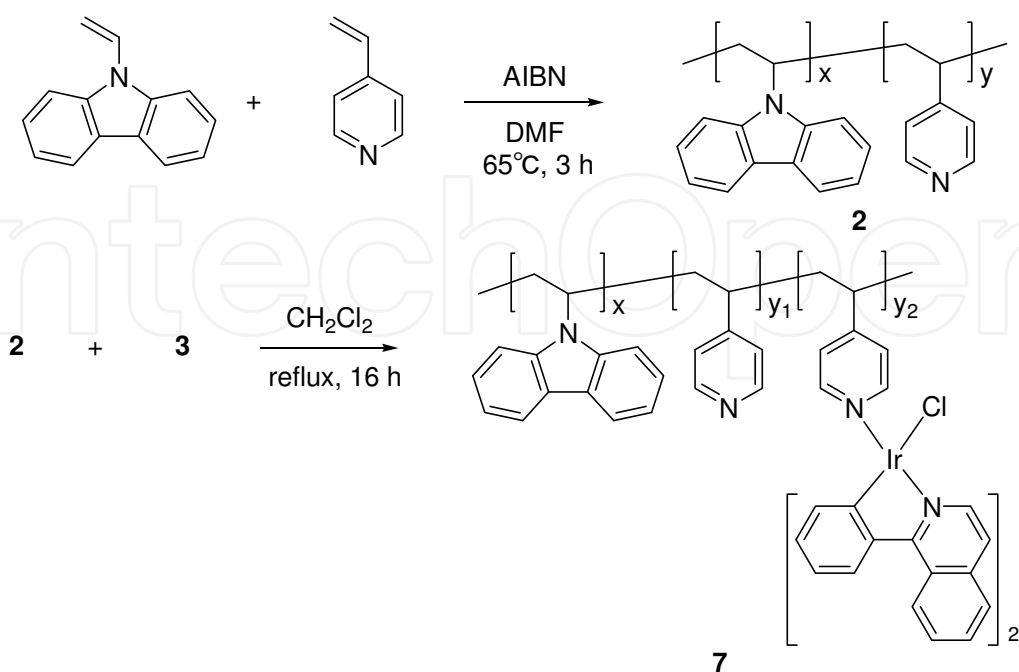
Scheme 6 depicts the synthetic procedure for the ligand copolymer **1** and the iridium-containing polymer **5**. MMA and Vp were copolymerized in the presence of benzoylperoxide (BPO) at 80 °C for 10 h to form the random copolymer **1**.¹⁰ The number-averaged molecular weight of **1** was 963000 g/mol, determined by size-exclusion chromatography (SEC) which was calibrated using polystyrene standards. The ¹H NMR spectroscopy of **1** revealed that the content of Vp was 23 mol%. These copolymers reacted with $[\text{IrCl}(\text{piq})_2]_2$ (**3**) in CH_2Cl_2 efficiently to form **5**, as a red compound. The expected quantity of the vinylpyridine iridium unit, $[\text{IrCl}(\text{piq})(\text{Vp})]$, in metallopolymer **5** was 49 wt%, which was calculated by the feed ratios of **3** and Vp in **1**. The luminescent polymer of platinum analog **6** was also prepared efficiently by the reaction of **1** with a platinum precursor, $[\text{PtCl}(\text{piq})_2]_2$ (**4**), in CH_2Cl_2 .

In these luminescent polymers, MMA were used as a comonomer in order to reveal the properties of luminescent modules. However, as noted below, the EL efficiencies of the devices including such metallopolymers were extremely low, because of the poor conductivity of MMA copolymer. Therefore, we used *N*-vinylcarbazole (Vc) as an alternative comonomer instead of MMA to improve the conductivity and luminescence property. Poly(*N*-vinylcarbazole) (PVK) has been known as a host material for OLED component, performing high conductivity due to closely arranged π conjugated sites which hang from the polyolefin backbone as a pendant group.¹¹ Scheme 7 depicts the synthetic procedure for the iridium-containing polymers **7a** and **7b** from ligand copolymers **2a** and **2b**, which have different Vp contents, 4.7 and 15 mol%, respectively. The content of Vp was determined by absorption coefficient ratio for PVK at 345 nm in CHCl_3 (Table 1). The ligand copolymers **2a** and **2b** were prepared in the presence of AIBN.¹² The reaction of these

copolymers with $[\text{IrCl}(\text{piq})_2]_2$ (**3**) in CH_2Cl_2 gave red solutions, similar to the prior experimental result forming **5** (Table 2). The quantities of the iridium unit, $[\text{IrCl}(\text{piq})_2(\text{Vp})]_{y2}$, content in the metallopolymers **7a** and **7b** were 8.4 and 25 wt%, which were determined by the feed ratios of **3** and Vp in **2a-b**.



Scheme 6. Preparation of **1**, **5**, and **6**.



Scheme 7. Synthesis of copolymers **2a-b**, and metallopolymers **7a-b**.

The MMA-copolymerized metallopolymer **5** and **6** were readily soluble in several organic solvents, such as CH₂Cl₂ and CHCl₃, whereas the Vc-copolymerized metallopolymer **7** had poor solubility toward these solvents. Figure 5 shows the ¹H NMR spectra for the monomeric complex **14**, **1**, and **5**. Broadened signals due to the aromatic protons of **1** appeared from δ 8.5 to 8.2 and from δ 7.1 to 6.6 (Figure 5 (b)), whereas new broad resonances were observed from δ 10.1 to 6.1 (c), assigned as aromatic protons of the incorporated iridium unit in **5**, which provided the similar set of signals to those corresponding to **14** (a). The result suggested that the iridium unit in **5** has the same chemical structure as that of **14**. The spectra for **6** were similarly observed. Several broadened signals assigned as aromatic groups of the iridium unit in **7** were also observed as shown in Figure 6 (b) and (d). These signals were shifted to the higher field when these signals were compared with those due to the monomeric analog **14** (Figure 6 (e)), probably due to the shielding effect of the surrounding aromatic groups of the carbazole side chain.

Ligand Polymer	Comonomer			Initiator (mmol)	Yield (%)	Vp Content (mol%)	Mn (×104 g/mol)	PDI	
	Vp (mmol)	Other (mmol)							
1	0.93	MMA	9.3	BPO	0.050	100	23	96	2.7
2a	1.0	Vc	20	AIBN	0.10	82	4.7	5.0	2.1
2b	2.0	Vc	20	AIBN	0.10	20	15	3.8	3.5

Table 1. Preparation of Ligand Polymers

Polymer Complex	Feed Polymer Ligand (Pyridine Content / mmol)		Feed Precursor Complex (Metal Content / mmol)		Yield (%)	[IrCl(piq) ₂ (Vp)] ₂ Content (wt%)
5	1	0.40	3	0.10	94	49
6	1	0.041	4	0.010	94	41
7a	2a	0.20	3	0.049	95	8.4
7b	2b	0.20	3	0.050	92	25

Table 2. Preparation of Metallopolymer

3. Preparation of metallopolymer containing conjugated polymer main chain

EL materials containing small molecules as doping luminescent compounds and conjugated polymers, such as PPV and PFO, have been developed as EL materials. Those performing more efficient luminescence have also been developed directly binding chromophores in the side chain of the conjugated polymers (Figure 4 and Scheme 3).^{5,7,7g} However, it is unknown that the luminescent iridium or platinum unit directory combines to the end of the conjugated polymers without breaking the π-conjugation, except one example.¹³ The conjugated binding between the host polymer and the guest chromophore is expected that intramolecular electron transfer occurs easily. Here we developed new

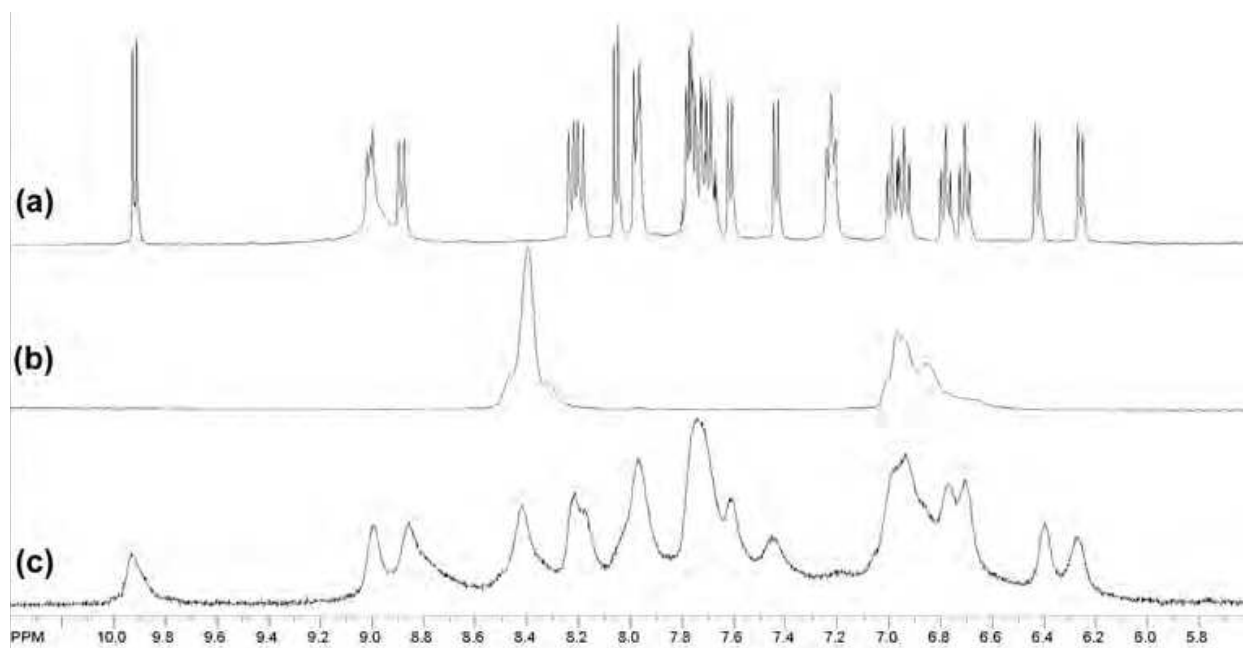


Fig. 5. ^1H NMR spectra in CD_2Cl_2 for (a) **14**, (b) ligand polymer **1**, and (c) metallopolymer **5** in the aromatic region.

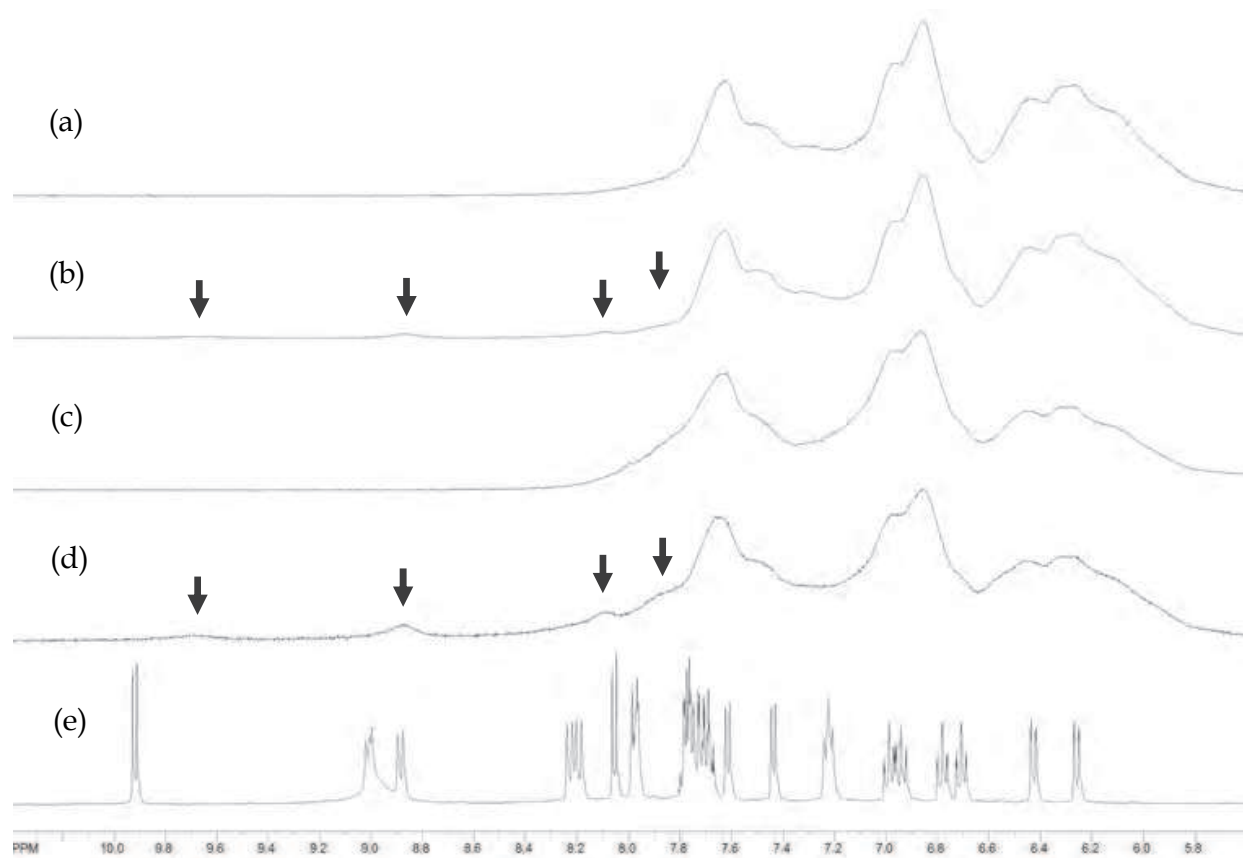
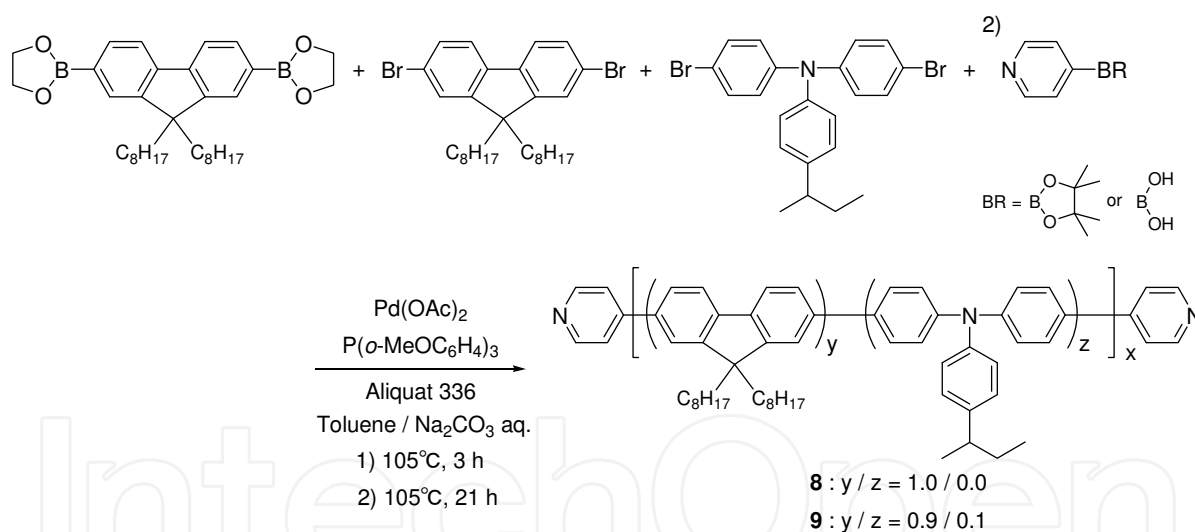


Fig. 6. ^1H NMR spectra in CD_2Cl_2 for (a) **2a**, (b) **7a**, (c) **2b**, (d) **7b** and (e) **14** in the aromatic region.

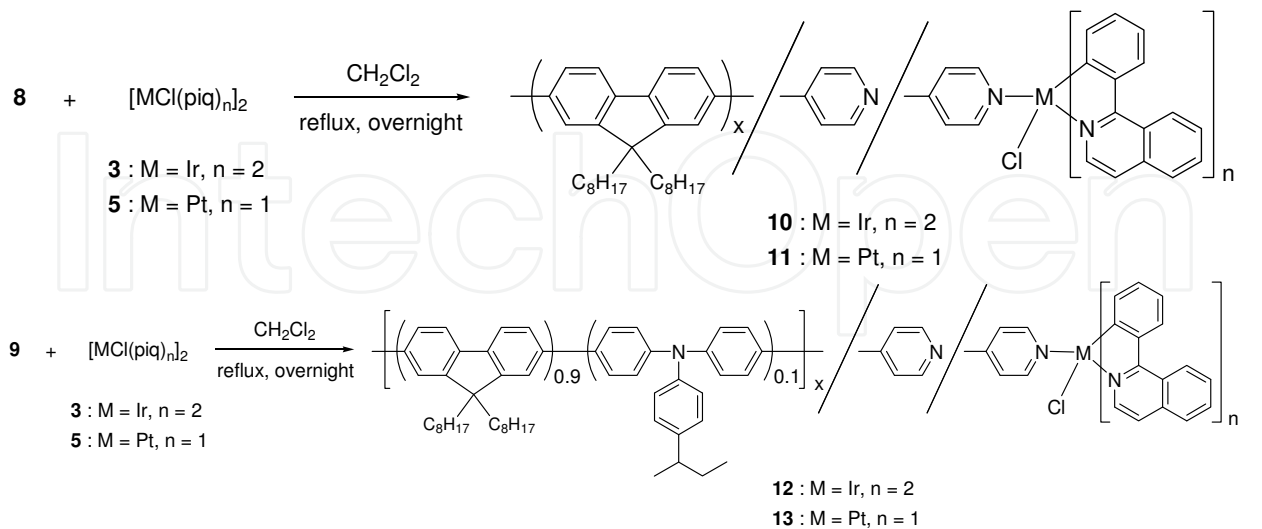
series of conjugated ligand polymers where a pyridyl group was introduced in the both ends of the polymers. As the previous preparation for the polyolefin metallopolymer, the luminescent 1-phenylisoquinoline iridium module was efficiently combined to the ligand polymers after polymerization. The procedures of the ligand polymers **8** and **9** and metallopolymer **10-13** are shown in Schemes 8 and 9. The conjugated polymer was prepared by the polycondensation reaction of two comonomers, 9,9-dioctylfluorene dibromide and bisboronic ester, mediated by a catalyst system using palladium acetate, tri(*o*-methoxyphenyl)phosphine, and sodium carbonate. Subsequent reaction of the obtained mixture with pyridylboronic acid pinacol ester or pyridylboronic acid formed the end-capped ligand polymers **8a** and **8b** in 34 or 53% yield. The content of the pyridyl group was 2.9 or 2.0 mol%, which was determined by ^1H NMR spectrum. On the other hand, a comonomer, 4-*sec*-butylphenyl-*N,N*-bis(4-bromophenyl)amine, was added to the polycondensation, resulted in the formation of triarylamine-containing ligand copolymers **9a** and **9b**. The yields, averaged molecular weights, and pyridyl-group contents are listed in Table 3. The reactions of the ligand polymers **8a** and **9a** with the iridium precursor **3** efficiently formed the metallopolymer **10** and **12**. The theoretical ratios of the iridium unit, $[\text{IrCl}(\text{piq})_2(\text{py})]$ in **10** and **12** were 1.7 and 1.7 wt%. The platinum analogs **11**, **13** were similarly synthesized from **8b**, **9b** and the platinum precursor **5**. The yields and the content ratios of iridium and platinum are listed in Table 4.



Scheme 8. Preparation of the conjugated ligand polymers **8** and **9**.

The metallopolymer **12** and **13**, in which the 4-*sec*-butylphenyl-diphenylamine group was included in the main chain, were readily soluble in several organic solvents, such as CH_2Cl_2 , and CHCl_3 , whereas the metallopolymer **10**, **11** had poor solubility toward these solvents. The ^1H NMR spectra for **10** and **12** demonstrated no existence of the precursor **3** but small amount of the iridium unit binding to the terminal as shown in Figure 7. In addition to the signals around δ 8.7 and from 7.0 to 8.5, small new signals, most of which agreed with those due to the monomeric iridium analog **14**, appeared, suggesting that the iridium unit in **10** and **12** has the similar structure to **14**. The appearance of the signal at δ 8.7 in the spectra for the products indicated that the free pyridyl group at the end of the polymers still remained in part, even after combination of the iridium module. The spectra

for the analogous polymers **11** and **13** containing platinum unit also showed the successful formation of the metallopolymers, in which the platinum unit has the similar structure to **15**.



Scheme 9. Preparation of the conjugated metallopolymers **10-13**.

Ligand Polymer	Comonomer				Yield (%)	Pyridine Content (mol%)	Mn (×104 g/mol)	PDI
	FlBO (mmol)	FlBr (mmol)	PABr (mmol)	PyBO (mmol)				
8a^a	5.1	6.2	0.0	1.8	34	2.9	2.9	1.4
8b	5.2	6.2	0.0	1.8	53	2.0	3.4	1.6
9a^a	5.2	5.0	1.2	1.8	28	3.5	3.1	1.3
9b	5.4	5.0	1.2	1.8	52	2.6	3.9	1.4

^a Pinacol ester instead of boronic acid was used as a coupling reagent in the synthesis of **8a** and **9a**.

Table 3. Preparation of the conjugated ligand copolymers.

Polymer Complex	Ligand Copolymer		Metal Precursor		Yield (%)	[IrCl(piq) ₂ (py)] Content (wt%)
		Pyridine Content (mmol)		Metal Content (mmol)		
10	8a	0.029	3	0.0051	80	1.7
11	8b	0.032	5	0.0056	76	1.1
12	9a	0.016	3	0.0030	68	1.7
13	9b	0.029	5	0.0055	34	1.0

Table 4. Preparation of the conjugated metallopolymers.

4. PL behavior of metallopolymers

The corresponding pyridine-substituted monomeric complexes of iridium and platinum (Figure 8 (a)) were also prepared for the first time in order to estimate the luminescent behavior of the metallopolymers containing the similar metal units,¹⁴ because polymer backbone sometimes influences luminescence of the metal units significantly both in the solid and solution states.^{8, 15} The structures of these complexes were well defined and the PL behaviors were compared with those of the metallopolymers.¹⁴ All the iridium and platinum complexes and polymers were irradiated at 462 and 433 nm, respectively, to observe the luminescence. As shown in Figure 8 (b), both the luminescent bands for the iridium and platinum complexes **14** and **15** were observed in almost the same area from 570 to 850 nm, although the low-energy absorption bands appeared in the different area (c).

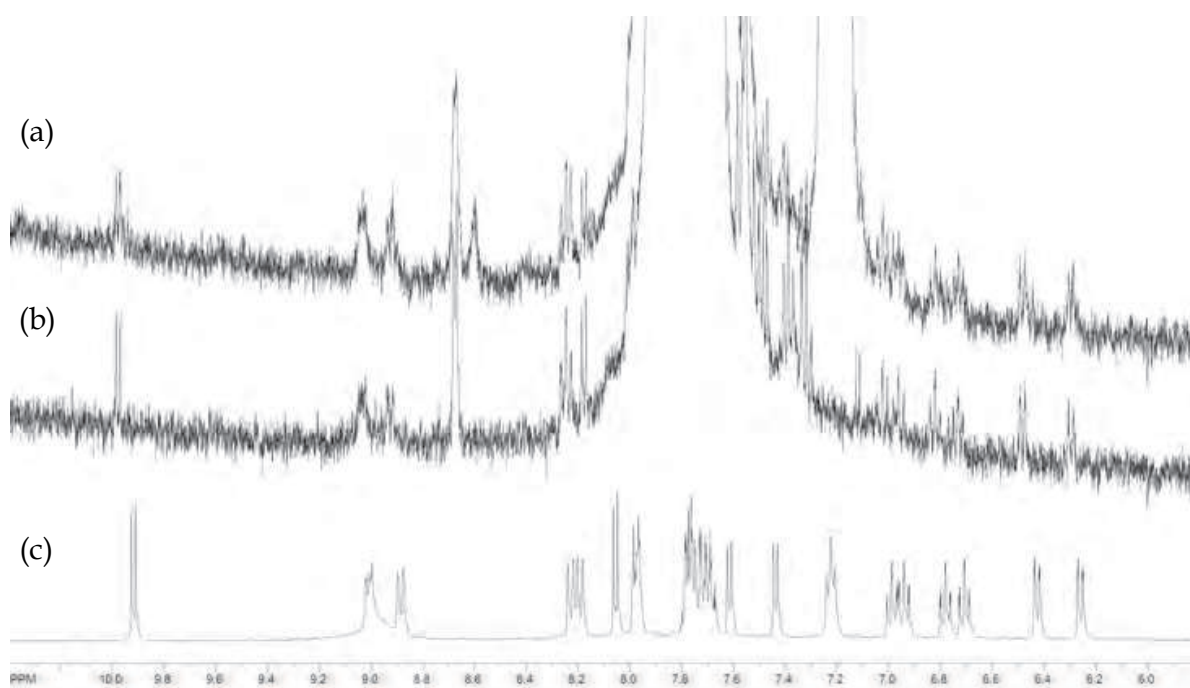


Fig. 7. ^1H NMR spectra in CD_2Cl_2 for (a) **12**, (b) **10** and (c) **14** in the aromatic region.

Figure 9 (a) and (b) show the PL spectra of the metallopolymers **5**, **6**, **7a** and **7b** in the CH_2Cl_2 solutions. Similar photoluminescent properties of the metallopolymers in the solutions to those of the monomeric metal analogs were observed when the concentrations of the metal units in the solutions were comparable. For example, red luminescence from **5** was observed and the wavelength at the maximum intensity was 620 nm. The PL spectra for **7** showed the emissions at ~ 620 nm from the incorporated $[\text{IrCl}(\text{piq})_2]$ unit. The intensity of the spectrum for the iridium polymer **5** was more than four times stronger than that for the platinum analog **6**. Lower intensity for **7a** than **7b** was coincident with the content ratios of the iridium unit in the metallopolymers (Table 2).

The PL spectra for the conjugated metallopolymers were shown in Figure 10. The spectra indicated that each structure of the metal unit was almost the same as that of the monomeric metal complex. The iridium-containing polymers **10** and **12** exhibited the similar luminescent spectra to that for the monomeric analog **14**, whereas the spectra for the platinum polymers **11** and **13** showed a characteristic strong band due to the conjugated

main chain under 570 nm in addition to the luminescence emitted by the platinum unit. The result of the latter suggested that the low-energy absorption band of the conjugated main chain, which was irradiated simultaneously, lies on almost the same wavelength area as that of the platinum unit. It was confirmed by the electronic spectra for these compounds.

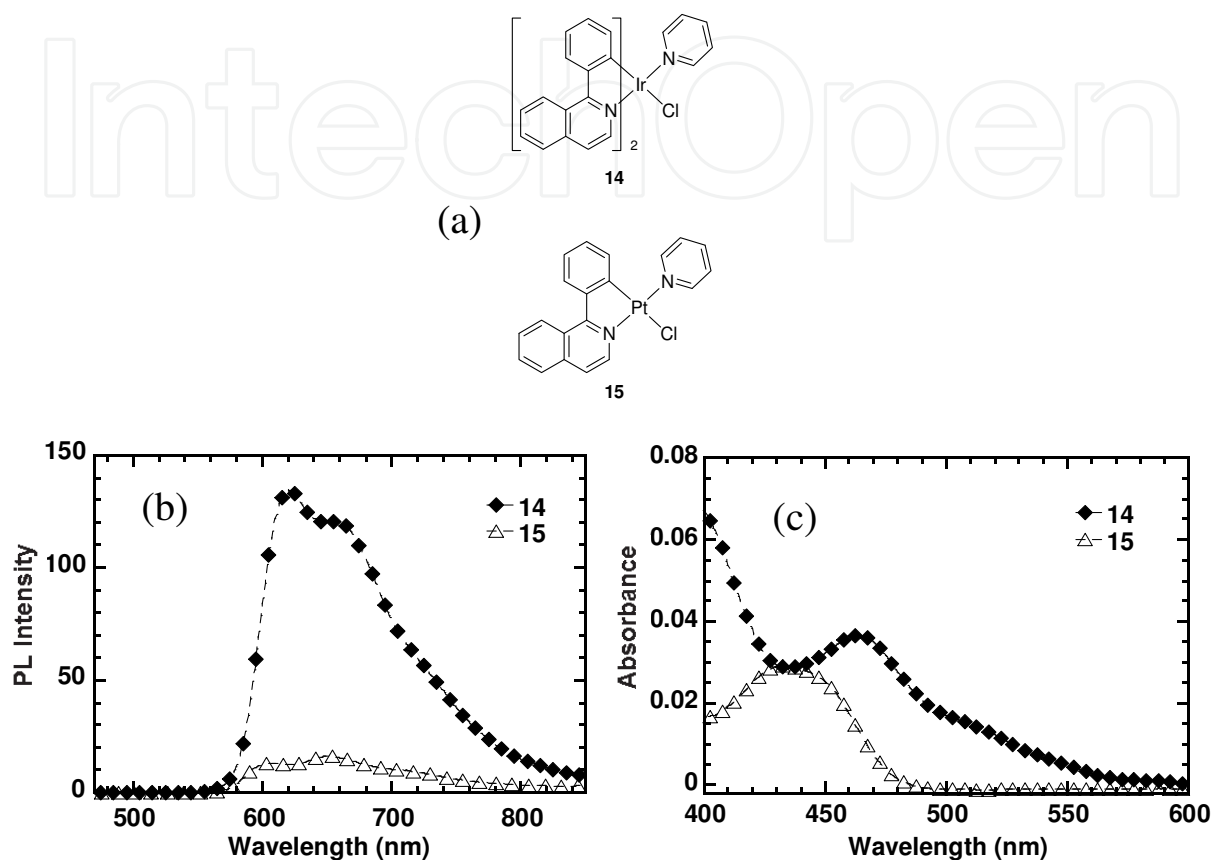


Fig. 8. (a) Structures, (b) PL and (c) UV-vis spectra of the monomeric complexes of iridium and platinum. (concentrations of the both complexes were 1×10^{-5} M.)

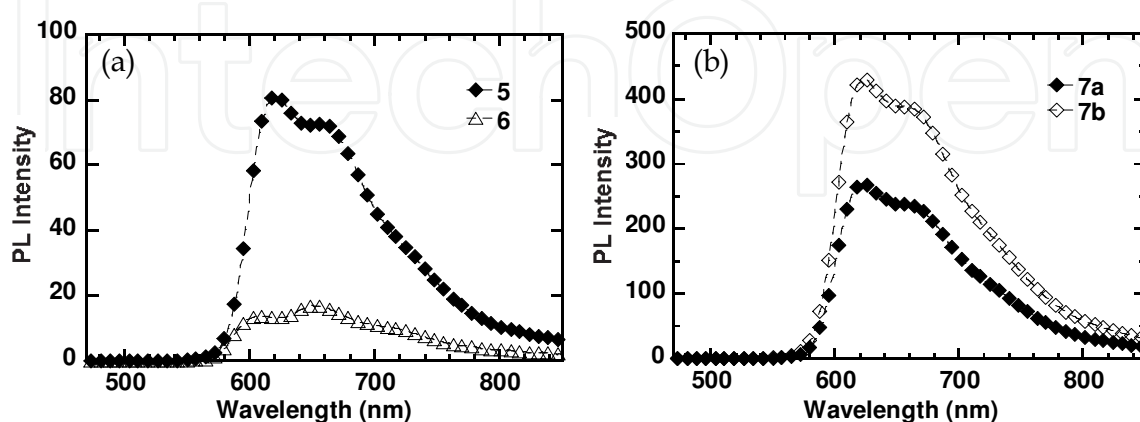


Fig. 9. PL spectra for (a) 5, 6 and (b) 7. Iridium polymers 5 and 7 and platinum polymer 6 were irradiated at 462 and 433 nm, respectively (metallopolymers 5, 6 were 0.05 g/L and metallopolymers 7 were 0.5 g/L).

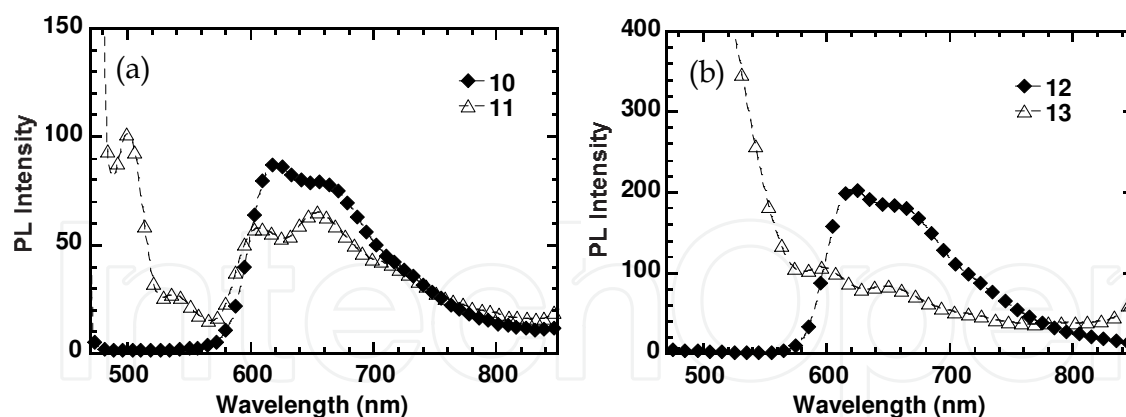


Fig. 10. PL spectra for (a) **10**, **11**, (b) **12** and **13** in CH_2Cl_2 . Iridium polymers **10** and **12** and platinum polymers **11** and **13** were irradiated at 462 and 433 nm, respectively (at 0.5 g/L).

5. EL behavior of the metallopolymers

EL behavior of devices containing the metallopolymers and the monomeric metal complexes was investigated. The metallopolymers composed of the conductive conjugated main chain exhibited the best performance among them, indicating that the structures of the polymer backbone closely affect the luminescence behavior, compared with those in the PL measurements.

We prepared several EL devices containing the luminescence layer of the metallopolymers as shown in Table 5. The first **device A** in entry 1 has only the iridium polymer **5** made from MMA / Vp copolymer, as the luminescence layer. The device performed 7.4 V of threshold voltage at 1 cd/m^2 and 0.026 cd/A (at 17.4 V) of maximum current efficiency, better than those of the previously reported iridium polymer made from 4-styryldiphenylphosphine copolymer, 13.2 V of threshold voltage at 1 cd/m^2 and 0.06 cd/A (at 20.0 V) of maximum current efficiency.⁸ The better performance in **device A** than the phosphine-based copolymer is probably derived from improved conductivity of the pyridine-based copolymer.

When a host polymer **16** was added to the luminescent layer of **5** to make **devices B-D**, the threshold voltage and maximum current efficiency were improved to some extent. The threshold voltage decreased particularly to the comparable level to the **devices Q** and **R**, which were based on the monomeric iridium analog **14**. However, the dominant luminescence in these devices was from the host polymer **16** at 435 nm, indicating that energy transfer from the host to the guest polymer may be disrupted by the non-conductive polyolefin main chain and methacrylate side chain. The **device E** did not emit at least up to 20 V, whereas the emission was slightly observed from the platinum unit but mainly from the host polymer **16** in **device F**. The behavior was different from the **devices T** and **U**, in which the luminescence from the doped platinum complex (605 and 650 nm) into **16** was detected. These results strongly suggest the presence of non-conductive copolymers involved in the metallopolymers lead to poor EL performance.

The **devices G** and **J**, in which the Vc copolymer was involved instead of MMA copolymer, showed unexpected high threshold voltage, despite PVK was known as conductive host polymer in EL devices.¹¹ The **device S**, containing the monomeric **14**-doped PVK, also performed high threshold voltage, suggesting that PVK does not perform enough

conductivity in the absence of conductive polymers. This high voltage was improved, when the conductive host polymer **16** was added to the luminescent layer. However, the maximum current efficiencies were not so different among **devices H, I and K, L**, in spite of the different iridium unit content ratios in these metallopolymer **7a** and **7b** (**7a** < **7b**, see Tables 1-3). Although the total performances of these devices based on the Vc copolymer were still not satisfactory, the energy transfer from the host polymer **16** to the metallopolymer occurred smoothly, leading to decrease of luminescence at 435 nm from the host **16**, in comparison with copolyMMA-based devices.

entry	Device ^a	Emitting Layer			Metal Unit Content ^b		V _{th} ^c (V)	$\eta_{c\ max}^d$ (cd/A, V)	λ_{max}^e (nm)
		Host ^f	Guest	Feed Ratio (Host / Guest)		(wt%)			
1	A	—	5	0 / 100	Ir	49	7.4	0.026, 17.4	635
2	B	16	5	80 / 20	Ir	9.8	5.0	0.063, 7.4	430
3	C	16	5	90 / 10	Ir	4.9	5.6	0.15, 8.2	435
4	D	16	5	95 / 5	Ir	2.5	4.8	0.091, 12.6	435
5	E	—	6	0 / 100	Pt	41	—	—	—
6	F	16	6	95 / 5	Pt	2.1	5.6	0.096, 9.6	435
7	G	—	7a	0 / 100	Ir	8.4	19.2	0.026, 20.0	625
8	H	16	7a	60 / 40	Ir	3.4	4.2	0.13, 6.8	430
9	I	16	7a	80 / 20	Ir	1.7	4.6	0.14, 7.6	430
10	J	—	7b	0 / 100	Ir	25	11.0	0.082, 20.0	630
11	K	16	7b	60 / 40	Ir	10	4.4	0.12, 6.4	430
12	L	16	7b	80 / 20	Ir	5	4.0	0.097, 5.8	430
13	M	—	10	0 / 100	Ir	1.7	4.0	1.14, 4.0	625
14	N	—	11	0 / 100	Pt	1.1	5.4	0.14, 7.6	605, 650
15	O	—	12	0 / 100	Ir	1.7	3.4	0.47, 3.6	620
16	P	—	13	0 / 100	Pt	1.0	5.8	0.36, 10.0	605, 650
17	Q	16	14	90 / 10	Ir	10	6.4	0.31, 9.2	625
18	R	16	14	95 / 5	Ir	5.0	5.0	0.30, 8.2	615
19	S	PVK	14	95 / 5	Ir	5.0	8.0	0.014, 19.8	630
20	T	16	15	90 / 10	Pt	10	10.0	0.024, 16.2	605, 650
21	U	16	15	95 / 5	Pt	5.0	6.8	0.048, 9.8	435

^a Device structure: ITO/PEDOT:PSS/Emitting layer/Ba/Al
^b Metal unit is [MCl(piq)_n(Py-)] (n = 2, Ir; n = 1, Pt) or the monomeric complex in the emitting layer.
^c Threshold voltage at 1 cd/m².
^d Maximum current efficiency.
^e The λ_{max} values correspond to the highest intensity peak in the EL spectrum at maximum current efficiency.

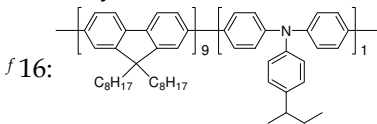


Table 5. EL properties of the devices containing the metallopolymer

The **devices M, N, O, and P** containing metal end-capped conjugated polymers provided satisfactory luminescence performances, compared with the other devices. As shown in Figure 11, negligible luminescence around 435 nm derived from the conjugated main chain was observed in the **devices M** and **O** containing iridium-capped polymers **10** and **12**, whereas considerable luminescence from the conjugated main chain appeared in the platinum-based **devices N** and **P**. We can conclude that iridium-based devices are superior to platinum-based ones in energy-transfer ability in this EL device system. The **device O** showed the highest performance as a red EL device among all the devices. It is of interest that the performances of the **devices M, O, N, P** excelled those of the **devices Q, R, T, U**, which contained the layer of the monomeric complex **14**- or **15**-doped copolymer **16**. We found that these **devices M, O, N, P** showed more than 1 V lower threshold voltages than those of the **devices Q, R, T, U**. These devices have the same structure except whether the metal chromophore is bound to the end of the host polymer (**M, O, N, P**) or exists independently (**Q, R, T, U**). We considered that direct combination of the conductive polymer and the metal unit led to facile electron transfer to the metal unit, resulting in low threshold voltages and high current efficiency of these devices. As for the iridium unit-containing devices, additional easy energy transfer from the host polymer to iridium caused the highest performance.

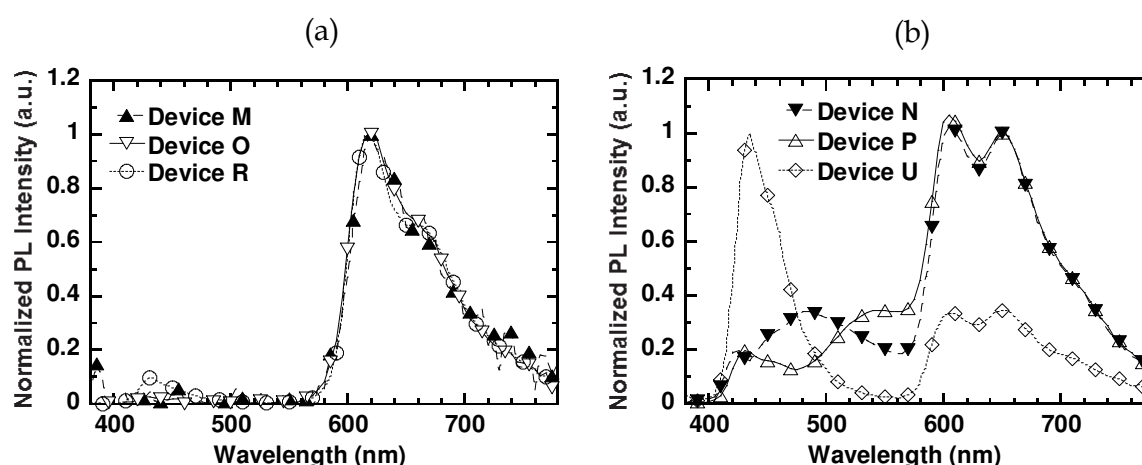


Fig. 11. EL spectra for (a) **devices M, O** and **R**, (b) **devices N, P** and **U**, of which the structures are shown in Table 5. (at 4.0, 4.0, 8.0, 8.0, 10.0, and 10.0 V, respectively) The origin of the small luminescent bands from 480 to 570 nm in (b) is not identified.

6. Conclusion

One of the most important factors to design new devices that contain complicated organic/inorganic/polymeric compounds is how to prepare the compounds easily and efficiently. Here we described the successful preparation of several luminescent polymer materials in a few steps, that contained the simple coordination of the metal module precursor to the pyridine-bound ligand polymers under mild conditions. After several attempts to investigate the EL behavior of the devices containing the obtained metallopolymer, we found that structure of backbone host polymer is quite important for efficient luminescence and low driving voltage in these devices. We also demonstrated that the good EL performance was provided when the guest unit directly bound to the host polymer.

7. Experimental details

7.1 Synthesis of pyridine-capped conjugated copolymers

As a typical example, into a 200-mL three-necked flask equipped with a condenser, 2.77 g (5.2 mmol) of 9,9-dioctylfluorene-2,7-bis(boronic acid ethylene glycol ester), 2.72 g (5.0 mmol) of 9,9-dioctyl-2,7-dibromofluorene, 0.551 g (1.2 mmol) of 4-(1-methylpropyl)-*N,N*-bis(4-bromophenyl)aniline, 0.79 g of methyltrioctylammonium chloride (Aliquat 336, made by Sigma-Aldrich Corporation), and 60 mL of toluene were placed. Under a nitrogen atmosphere, 2.2 mg of palladium diacetate and 12.9 mg of tris(2-methoxyphenyl)phosphine were added to the solution, and the solution was heated to 95°C. While a 17.5 wt% sodium carbonate aqueous solution (16.5 mL) was dropped to the obtained solution over 30 minutes, the solution was heated to 105°C, and subsequently stirred at 105°C for 3 hours. Then, 369 mg of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine dissolved in toluene (30 mL) was added, and the mixture was stirred at 105°C for 21 hours. After the aqueous layer was removed, 3.65 g of sodium *N,N*-diethyldithiocarbamate trihydrate and 36 mL of water were added, and the solution was stirred at 85°C for 2 hours. An organic layer was separated and washed with water (78 mL, twice), a 3 wt% aqueous acetic acid (78 mL, twice), and then water (78 mL, twice). The organic layer was dropped to methanol to form precipitates, which were filtrated and dried to obtain a solid. The residual solid was dissolved in toluene (186 mL), and the solution was passed through a silica gel / alumina column, where toluene was passed in advance. The filtrate was concentrated under reduced pressure and dropped into methanol, and a precipitate was filtered to obtain ligand polymer **9a** (1.26 g). The number-averaged molecular weight M_n was 3.1×10^4 g/mol, which was determined by SEC calibrated with polystyrene standards.

7.2 Synthesis of conjugated iridium polymers

As a typical example, under an inert-gas atmosphere, a mixture of $[\text{IrCl}(\text{piq})_2]_2$ (**3**) (0.0038 g, 0.0030 mmol) and pyridine-capped copolymer **9a** (0.243 g, containing 0.016 mmol of pyridine) in CH_2Cl_2 (6 mL) was refluxed for 16 h. After cooling to room temperature, the resulting solution was poured into hexane to afford a precipitate, which was filtered and washed with hexane and dried under reduced pressure to obtain light orange powder **10** in 80 % yield ($M_n = 3.3 \times 10^4$ g/mol).

8. Acknowledgement

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9. Abbreviations

PL: photo-luminescent
EL: electro-luminescent
PLED: polymer light-emitting diode
OLED: organic light-emitting diode
PPV: polyphenylene vinylene
PVK: poly(vinylcarbazole)
PFO: poly(9,9-di-n-octyl-2,7-fluorene)

MMA: methyl methacrylate

Vp: 4-vinylpyridine

piq: 1-phenylisoquinoline

SEC: size-exclusion chromatography

Vc: N-vinylcarbazole

AIBN: azobisisobutyronitrile

BPO: benzoylperoxide

FlBO: 9,9-dioctylfluorene-2,7-bis(boronic acid ethylene glycol ester)

FlBr: 9,9-dioctyl-2,7-dibromofluorene

PABr: 4-sec-butylphenyl-N,N-bis(4-bromophenyl)amine

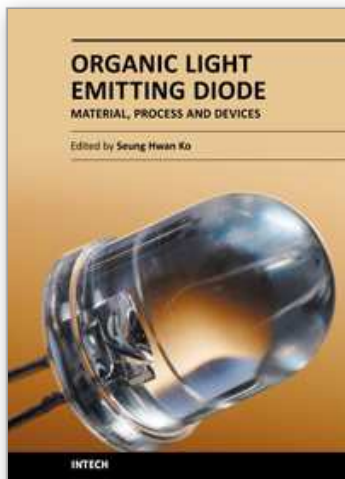
PyBO: 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine boronic acid

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