Synthesis and Luminescence Behavior of Cyclometallated Iridium Complexes Bound to a Phosphine-Containing Polymer Ligand

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Abstract

We successfully developed two types of phosphorescent cyclometallated iridium complexes, which are two different red-luminescent iridium complexes bearing one and two phosphine-containing copolymers used as polymer ligands, and investigated their PL behavior. The phosphine copolymer ligand made from methyl methacrylate (MMA) and 4-styryldiphenylphosphine can be used as an anchor bound to the iridium luminescent units to form the metallopolymer facilely. The solubility of the bisphosphine iridium polymer complex towards standard solvents was extremely low due to maybe its highly cross-linking structure. Monophosphine metallopolymer exhibited red luminescence around 600 nm as expected from the result of the corresponding complex having non-polymer phosphine ligands, whereas luminescence of the bisphosphine polymer complex performed different behavior in the emitting wavelength and its intensity from that having non-polymer bisphosphine complex. Interestingly, emission intensity of the bisphosphine polymer complex toward the iridium content strongly depends upon the molecular weight of the polymer ligands.

1.　INTRODUCTION

In recent, much attention is concentrated on developing polymeric light-emitting diodes (PLED), since fabrication of a thin-film devices using the solution of polymeric materials, such as spin-coating, screen printing, and ink-jet printing, are superior in process cost and product efficiency than those of the organic light-emitting diodes (OLED). These film-preparing techniques may be powerful processes manufacturing large-area and fine-pixel EL displays.

As shown in Figure 1, two types of PLED materials are well known as follows: (1) polymers in which luminescent small molecules are doped into polymer hosts such as PVK (poly(vinyl-carbazole)) and PFO (poly(9,9-di-n-octyl-2,7-fluorene)),[1-6] and (2) polymers having luminescent units in their main chain or side chain. In the former polymer, phase separation and crystallization of the small molecules in the polymer matrix may reduce the luminescence efficiency and prevent uniform emission all over the films. Thus, the latter polymer has now become attractive, although development of fine, suitable PLED is delayed because of the difficulty in regulating structure of PLED precisely. In the latter poly-

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mers, two types of luminescent polymers are known – π–conjugated polymers such as polyfluorenes and polyphenylene-vinylenes (PPV),[7] and non-conjugated polymers in which small OLED materials are bound to the polymer main-chain or side-chain.

In recent studies, phosphorescent metal complexes of which emitting efficiency is 4 times higher than that of fluorescent molecules are considered as the most useful OLED units binding to the polymer, and most of the luminescent metallopolymers (D) are made from metal-containing monomers (B).[8-10] (Figure 2, *Method A*) However, a process by which the emitting polymer (D) is formed by the reaction of a metal compound with a polymer ligand (C) made from a ligand-unit-containing monomer (A) (Figure 2, *Method B*) is rare to the best of our knowledge.[11,12]

From the viewpoint of the preparative procedure for metallopolymers, in the polymer-growth conditions of *Method A*, their formation is sometimes unsuccessful because of the elimination of metals or metal-mediated side-reactions, whereas, in contrast, synthetic procedures of various polymer-ligands (including copolymers) (C) in *Method B* have been established in many cases.[13] Thus, polymer-ligand synthesis in *Method B* may facilitate preparing metallopolymers (D) with various molecular weights. Moreover, *Method B* may make regulating polymer structure precisely facile. Phosphine-containing polymers which are prepared by polymerization of vinyl-group-attached triphenylphosphine monomer have already been applied to a number of materials, such as the precursor for phosphorus-containing functional polymers[13,14] and polymer ligands bound to metal catalysts.[15] However, polymer-bound photoluminescent iridium complexes linked with phosphines have never been reported. Although phosphines are rarely used as the ligands binding to luminescent metal com-
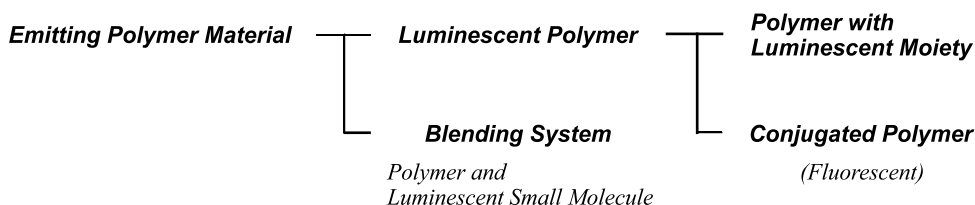
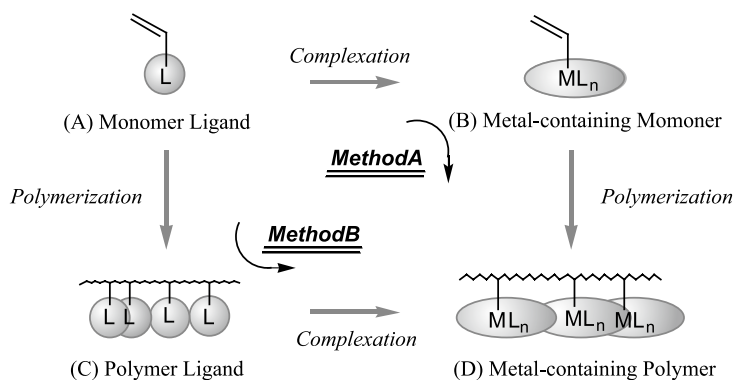

Figure 1.   Classification of emitting polymer material.

Figure 2.   Preparation method of metal-containing polymer.

plexes in OLED,[16] these are the most versatile and useful ligands for coordinating iridium atoms among a number of ligands in the metal complexes.[17]

For developing the OLED light emitting material, an iridium(III) complex, which performs high quantum efficiency, is commonly well-used. We found that an iridium complex having two phosphorus ligands at the *trans* position reported by R. B. Crabtree, et al.[18] emitted red light when it was irradiated at 367 nm [Figure 3 (a)]. Moreover, similar red-luminescent 1-phenylisoquinolinato iridium complex bearing only one phosphine ligand was newly prepared [Figure 3(b)].
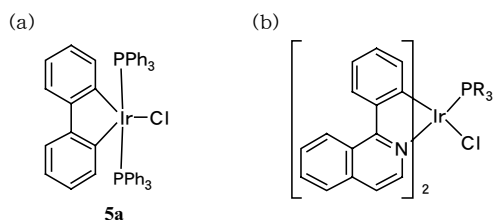

Figure 3. Attention red-luminescent Ir(III) complex with phosphine ligand.

Here we report a novel and convenient synthetic method for luminescent iridium-containing polymers, which was prepared by way of *Method B* using polymer ligands bearing phosphines easily prepared by standard radical polymerization. The bisphosphine or monophosphine iridium unit was incorporated with the polymer ligand by way of the usual organometallic process. Then, the photo luminescence (PL) behavior of these metallopolymers in the solid or solution state was investigated in detail.

2．EXPERIMENTAL

2-1. Synthesis of Luminescent Iridium Polymers

2-1-1. Synthesis of Copolymer Ligands

Copolymer ligands 1a-f were prepared with comonomers, MMA and 4-styryldiphenylphosphine (4-SDP), in a similar manner to the literature;[13] typically, MMA (2.0 mL, 19 mmol), 4-SDP (0.58 g, 2.0 mmol) and azobis(isobutylo)nitrile (AIBN) (0.35 g, 2.1 mmol) were mixed in 1,4-dioxane (2.0 mL), and the flask was placed into a 60℃ water bath and stirred for 2 h. The resultant polymer was precipitated into methanol, dissolved again in 1,4-dioxane, and precipitated in hexane (2 times). Copolymer 1a was dried under reduced pressure. Yield: 1.24 g, 52.0 %.

^{1}H NMR (400 MHz, CD_2Cl_2), δ 6.6-7.8 (ArH), 2.2-3.8 (OCH_3), 1.1-2.2 (CH and CH_2), 0.3-1.1 (α-CH_3); ^{31}P NMR (162 MHz, CD_2Cl_2), δ -5.7--5.1 (br, P).

Other copolymers 1b-f were synthesized with changing the amount of 4-SDP. Detailed preparative data for 1a-f are listed in Table 1. The molecular weight, M_n, and the polydispersity, M_w/M_n, of the copolymers were determined by size exclusion chromatography (SEC). Calibration was carried out using polystyrene standard. The 4-SDP content in the copolymers was determined from the integrated signal ratio of the ^{1}H NMR resonances at δ 6.6-7.8 (aromatic) and δ 0.3-1.1 (α-CH_3).

Table 1.   Preparation of Ligand Polymers 1a-f.

Ligand polymers	MMA (ml)	4-SDP (g)	AIBN (g)	Yield (%)	4-SDP content [a] (mol%)	M_n [b]	PDI [b]
1a	10	3.5	0.085	34	9	14 800	2.1
1b	2	0.58	0.070	46	13	47 900	9.1
1c	2	0.58	0.35	52	22	13 800	2.2
1d	2	0.54	0.34	64	14	19 300	2.3
1e	2	0.54	0.23	57	16	25 300	2.7
1f	2	1.08	0.43	91	22	11 900	2.5

[a] The actual compositions of the copolymers were determined by ^{1}H NMR spectroscopy. The ratio of the integration of the protons from the aromatic rings to the α-CH$_3$ hydrogen atoms was used to determine the mole percent of 4-SDP in each copolymer.

[b] M_n values were determined by SEC analysis in THF calibrated with polystyrene standards.

2-1-2. Synthesis of Bisphosphine Iridium-Containing Polymers

Bisphosphine iridium-containing polymers 2a-e, 3a-e, 4a-j were prepared in a similar manner to synthesis of 5a; typically, a mixture of [Ir(cod)(biph)Cl]$_2$[18] (7.3 mg, 0.0075 mmol) and phosphine polymer 1a (0.20 g, corresponding to 0.15 mmol of phosphorus) in CH$_2$Cl$_2$ (4.0 mL) was stirred at room temperature for 24h under N$_2$ in a screw-cap vial. The polymer was precipitated into hexane, filtered and dried under reduced pressure. The resultant polymer, 2a, was suspended in CH$_2$Cl$_2$, a small amount of hexane was added, and filtered (several times). Other metallopolymers 2b-e, 3a-e, 4a-j were synthesized with changing the amount of the iridium precursor, [Ir(cod)(biph)Cl]$_2$. The amount of reagents and content of iridium in the metallopolymers are shown in Table 2.

Although these metallopolymers were hardly soluble in various solvents, the polymer 3c was fortunately soluble in CD$_2$Cl$_2$ and the ^{1}H and ^{31}P NMR spectral measurements were carried out.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$), δ 6.1-7.8 (ArH), 2.2-4.0 (OCH$_3$), 0.2-2.2 (CH, CH$_2$, α-CH$_3$); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$), δ 21.85 (s, Ir-P), -5.43 (s, ArP)

The iridium contents of the metallopolymers, 2a-e, 3a-e, 4a-j, were determined by residue in an ignition test, which was calibrated with the complex 5a.

2-1-3. Synthesis of Bisphosphine Iridium Complexes

In order to compare with the luminescent behavior of the metallopolymers, iridium non-polymer complexes 5a-f were all prepared in a similar manner to the literature;[18] typically, a mixture of [Ir(cod)(biph)Cl]$_2$ (0.097g, 0.10 mmol) and triphenylphosphine (0.10g, 0.40 mmol) in CH$_2$Cl$_2$ (3.0 mL) was stirred at room temperature for 24 h. After the majority of the CH$_2$Cl$_2$ was removed under reduced pressure, diethyl ether was added. The orange precipitate was filtered and washed with cooled CH$_2$Cl$_2$ and dried under reduced pressure. Complex 5a was purified by recrystallization from CH$_2$Cl$_2$/Et$_2$O.

5b: orange powder; 71.7% yield; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.34 (br s, 4H, Ar), 7.29 (d, 8.0 Hz, 2H, biph), 7.21 (d, 7.6 Hz, 4H, Ar), 7,15 (br s, 8H, Ar), 7,10-6.98 (m, 12H, Ar), 6.43 (t, 7.2 Hz, 2H, biph), 6.26 (dt, 1.2 and 7.5 Hz, 2H, biph), 6.18 (dd, 1.2

Table 2.　Preparation of Metallopolymers 2a-e, 3a-e, 4a-j; Quantity of the Used Polymer Ligand 1a-c and [Ir(cod)(biph)Cl]$_2$, Feed Ratio, and Observed Ir Content.

polymer complex	used polymer ligand		used [Ir(cod)(biph)Cl]$_2$		feed Ir / P ratio	determined Ir content (mmol/g)[a]	determined Ir / P ratio
	(mg)	(mmol)	(mg)	(mmol)			
2a	1a 197	0.15	7	0.008	0.1	0.059	0.08
2b			15	0.015	0.2	0.084	0.11
2c			22	0.023	0.3	0.139	0.19
2d			29	0.030	0.4	0.187	0.25
2e			37	0.038	0.5	0.233	0.32
3a	1b 141	0.15	4	0.004	0.05	0.078	0.07
3b			7	0.008	0.1	0.145	0.14
3c			15	0.015	0.2	0.191	0.19
3d			22	0.023	0.3	0.282	0.28
3e			37	0.038	0.5	0.358	0.36
4a	1c 97	0.15	4	0.004	0.05	0.138	0.09
4b			7	0.008	0.1	0.224	0.15
4c			15	0.015	0.2	0.267	0.18
4d			22	0.023	0.3	0.348	0.24
4e			37	0.038	0.5	0.418	0.29
4f			44	0.045	0.6	0.513	0.37
4g			51	0.053	0.7	0.601	0.44
4h			59	0.060	0.8	0.610	0.45
4i			66	0.038	0.9	0.613	0.45
4j			73	0.075	1.0	0.628	0.46

[a] Ir content of the metallopolymers was determined by residue on ignition test.

and 7.2 Hz, 2H, biph), 2.35 ppm (s, 6H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.93, 140.07, 138.07, 134.90, 134.34, 132.17, 129.67, 129.43, 128.56, 127.36, 123.23, 121.42, 120.64, 21.39 ppm; ^{31}P NMR (162 MHz, CDCl$_3$): δ 22.55 ppm (s, 2P, PAr$_3$). Anal. Calcd for IrC$_{50}$H$_{42}$ClP$_2$: C, 64.40; H, 4.54%. Found: C, 64.70; H, 4.66%.

5c: orange powder; 46.3% yield; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.50 (br s, 4H, Ar), 7.33 (d, 8.0 Hz, 2H, biph), 7.16 (t, 6.8 Hz, 4H, Ar), 7.12-6.96 (m, 16H, Ar), 6.60 (d, 8.8 Hz, 4H, Ar), 6.41(t, 7.4 Hz, 2H, biph), 6.26 (dt, 1.2 and 7.4 Hz, 2H, biph), 6.16 (dd, 1.2 and 7.6 Hz, 2H, biph), 2.97 ppm (s, 12H, CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.97, 151.24, 138.49, 136.55, 134.07, 132.23, 130.70, 128.92, 127.07, 123.07, 121.11, 120.42, 114.38, 111.34,

40.01 ppm; ^{31}P NMR (162 MHz, CDCl$_3$): δ 21.40 ppm (s, 2P, PAr$_3$). Anal. Calcd for IrC$_{52}$H$_{49}$ClP$_2$: C, 63.05; H, 4.90; N, 2.83%. Found: C, 62.78; H, 4.91; N, 2.84%.

5d: orange powder; 63.7% yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.36- 7.15 (m, 22H, Ar and biph), 7.11 (t, 7.2 Hz, 8H,Ar), 6.64 (dd, 10.8 and 17.6 Hz, 2H, vinyl), 6.43 (t, 7.2 Hz, 2H, biph), 6.26 (dt, 1.2 and 7.6 Hz, 2H, biph), 6.17 (dd, 1.2 and 7.6 Hz, 2H, biph), 5.74 (d, 17.6 Hz, 2H, vinyl), 5.26 ppm (d, 10.8 Hz, 2H, vinyl); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.91, 138.78, 137.90, 136.31, 134.85, 134.48, 132.11, 129.66, 129.20, 127.52, 125.38, 123.34, 121.58, 120.81, 115.29 ppm; ^{31}P NMR (162 MHz, CDCl$_3$): δ 22.56 ppm (s, 2P, PAr$_3$). Anal. Calcd for IrC$_{52}$H$_{42}$ClP$_2$: C, 65.30; H, 4.43%. Found: C, 65.02; H, 4.50%.

5e: orange powder; 37.1% yield; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.51 (d, 7.2 Hz, 4H, Ar), 7.46-7.10 (m, Ar and biph), 6.44 (t, 7.4 Hz, 2H, biph), 6.28 (dt, 1.6 and 7.6 Hz, 2H, biph), 6.16 (dd, 1.2 and 7.6 Hz, 2H, biph); ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.95, 142.19, 140.47, 138.09, 134.70, 132.12, 129.81, 129.65, 128.74, 127.67, 127.13, 126.10, 123.39, 121.60, 120.84 ppm; ^{31}P NMR (162 MHz, CDCl$_3$): δ 22.75 (s, 2P, PAr$_3$). Anal. Calcd for IrC$_{60}$H$_{46}$ClP$_2$: C, 68.20; H, 4.39%. Found: C, 67.91; H, 4.61%.

5f: orange powder; 17.6% yield; ^{1}H NMR (400 MHz, Acetone-d$_6$): δ 11.3 (br s, CO$_2$H), 7.68 (d, 7.6 Hz, 4H, Ar), 7.56-7.40 (m, 14H, Ar), 7.31 (t, 7.2 Hz, 8H, Ar), 7.10 (br s, 4H, Ar), 6.46 (t, 7.2 Hz, 2H, biph), 6.29 (d, 7.6 Hz, 2H, biph), 6.24 (d, 7.6 Hz, 2H, biph); ^{13}C NMR (100 MHz, Acetone-d$_6$): δ 166.29, 155.04, 137.82, 135.00, 134.04, 132.26, 131.40, 130.46, 129.23, 128.10, 127.98, 123.50, 121.96, 120.91 ppm; ^{31}P NMR (162 MHz, Acetone-d$_6$): δ 23.05 (s, 2P, PAr$_3$). Anal. Calcd for IrC$_{50}$H$_{38}$O$_4$ClP$_2$: C, 60.51; H, 3.86%. Found: C, 60.40; H, 4.03%.

2-1-4. Synthesis of Monophosphine Iridium Polymer Complexes

The monophosphine iridium polymer complexes 6a-f, 7a-e, 8a-e were synthesized in a similar manner to synthesis of 9; typically, synthetic method for 6e was as follows. Under an inert atmosphere, a mixture of [Ir(piq)$_2$Cl]$_2$[19] (piq: 1-phenylisoquinolinato) (53.7 mg, 0.042 mmol) and the phosphine copolymer 1d (0.134 g, containing 0.15 mmol of phosphorus) in CH$_2$Cl$_2$ (10.0 mL) was stirred in a screw bial at room temperature for 12 h. The resulting solution was poured into hexane to afford a precipitate, which was filtered and washed with cooled CH$_2$Cl$_2$ and dried under reduced pressure.

^{1}H NMR (400 MHz, CD$_2$Cl$_2$), δ 9.3-9.5 (ArH), 8.8-9.0 (ArH), 8.5-8.8 (ArH), 8.0-8.3 (ArH), 6.4-8.0 (ArH), 6.1-6.4 (ArH), 6.0-6.1 (ArH), 2.2-3.8 (OCH_3), 0.3-2.2 (CH, CH_2, α-CH_3); ^{31}P NMR (162 MHz, CD$_2$Cl$_2$), δ 28.0-28.8 (br, P = O), -2.9--1.8 (br, Ir-P), -5.6--5.1 (br, P)

Other metallopolymers 6b-f, 7a-e, 8a-e were synthesized with changing the ratios of the amount of [Ir(piq)$_2$Cl]$_2$ to the polymer ligand. The details were shown in Table 3. The iridium content in the metallopolymers 6a-f, 7a-e, 8a-e were determined from the integral ratios of the ^{31}P NMR resonances.
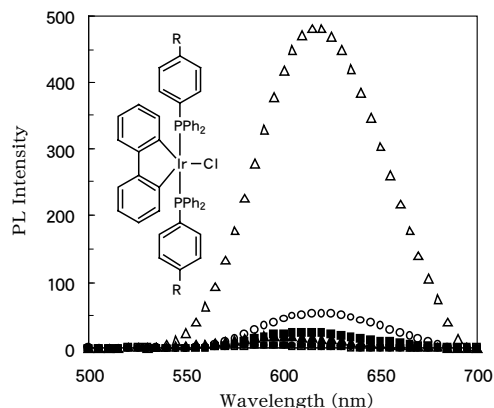
	R	λ_{Em} (nm)	λ_{Ex} (nm)
5a	H	618	367
5b	Me	615	368
5c	NMe$_2$	577	362
5d	CH=CH$_2$	596	366
5e	Ph	584	361
5f	CO$_2$H	601	368

Figure 4. Solid-state emission spectra for complexes 5a-f measured at 298K. Symbols indicate the complexes: △, 5a; ○, 5b; □, 5c; ▲, 5d; ●, 5e; ■, 5f.

Table 3. Preparation of Metallopolymers 6a-f, 7a-e, 8a-e; Quantity of the Used Polymer Ligand 1d-f and $[Ir(piq)_2Cl]_2$, Feed Ratio, and Observed Ir Content.

polymer complex	used polymer ligand			used $[Ir(piq)_2Cl]_2$		feed Ir / P ratio	determined Ir content (mmol/g)[a]	determined Ir / P ratio
		(mg)	(mmol)	(mg)	(mmol)			
6a	1d	134	0.15	3.9	0.003	0.04	0.030	0.03
6b				7.6	0.006	0.08	0.076	0.07
6c				15	0.012	0.16	0.168	0.17
6d				31	0.024	0.32	0.308	0.34
6e				54	0.042	0.56	0.481	0.62
6f				75	0.059	0.79	0.631	0.94
7a	1e	121	0.15	4.5	0.004	0.05	0.019	0.02
7b				9.5	0.007	0.10	0.118	0.10
7c				19	0.015	0.20	0.186	0.17
7d				38	0.030	0.40	0.333	0.35
7e				67	0.053	0.70	0.588	0.76
8a	1f	96	0.15	5.0	0.004	0.05	0.074	0.05
8b				9.2	0.007	0.10	0.120	0.08
8c				20	0.015	0.20	0.297	0.24
8d				39	0.030	0.40	0.424	0.38
8e				67	0.053	0.70	0.681	0.78

[a] Ir content of the metallopolymers was determined by ^{31}P NMR spectroscopy. The ratio of the integration of the phosphorus from the phosphine complexes to the phosphine and phosphine oxide atoms was used to determine the Ir content in each copolymer.

2-1-4. Synthesis of Monophosphine Iridium Complexes

In order to compare with the luminescent behavior of the metallopolymers, iridium non-polymer complexes 9 was prepared. Under an inert atmosphere, $[Ir(piq)_2Cl]_2$ (0.13 g, 0.10 mmol) and triphenylphosphine (0.11 g, 0.040 mmol) were added to a 20 mL Schlenk tube and dissolved in CH_2Cl_2 (10 mL). The solution was stirred at ambient temperature for 15 h. The solvent in the resulting dark red solution was removed under reduced pressure. The residual solid was recrystallized from CH_2Cl_2/hexane, giving 9 as brownish orange crystals (0.13 g, 72 % yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.42 (d, 6.8 Hz, 1H, Ar), 8.95 (d, 8.4 Hz, 1H, Ar), 8.70 (d, 6.4 Hz, 1H, Ar), 8.67 (d, 8.0 Hz, 1H, Ar), 8.19 (d, 8.0 Hz, 1H, Ar), 8.12 (d, 8.0 Hz, 1H, Ar), 7.89 (d, 7.2 Hz, 1H, Ar), 7.82 (d, 7.2 Hz, 1H, Ar), 7.79-7.73 (m, 2H, Ar), 7.69-7.62 (m, 2H, Ar), 7.20-7.11 (m, 11H, Ar), 7.03-6.93 (m, 8H, Ar), 6.71 (t, 7.2 Hz, 1H, Ar), 6.59 (t, 7.4 Hz, 1H, Ar), 6.28 (d, 7.6 Hz, 1H, Ar), 6.06 (dd, 6.4 and 6.4 Hz, 1H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.01, 169.96, 167.18, 163.31, 162.35, 151.63, 151.57, 147.14, 147.06, 144.74, 144.43, 142.58, 136.33, 136.21, 133.94, 133.84, 132.01, 130.59, 130.24, 130.08, 129.92, 129.69, 129.65, 129.28, 129.26, 128.78, 128.76, 127.40, 127.06, 126.98, 126.67, 126.48, 126.41, 126.06, 125.91, 125.14, 121.40, 120.04, 119.68, 119.25 ppm; ^{31}P NMR (162 MHz, $CDCl_3$): δ -1.45 ppm (s, P)

2-2. PL Measurement

Photoluminescence (PL) spectra were re-
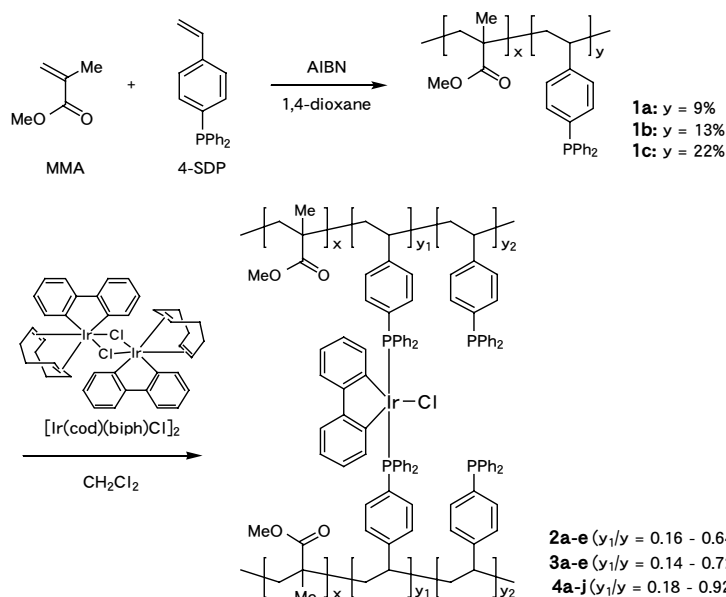
Scheme 1. Preparation of metal-containing polymer 2a-e, 3a-e, 4a-j.

corded on a JASCO FP-750 spectrofluorometer. The measurement of hardly soluble bisphosphine iridium polymer complexes was carried out in the solid state with a JASCO FDA-430 solid sample holder. The PL spectra of monophosphine iridium polymer complex were measured in the 0.1g/L CH_2Cl_2 solution.

3. RESULTS AND DISCUSSION

3-1. Synthesis and Characterization of Bisphosphine or Monophosphine Iridium Polymer Complexes

A synthetic route for bisphosphine iridium polymer complex is shown in Scheme 1. Copolymerization of MMA and 4-SDP in 1,4-dioxane was carried out in the presence of AIBN as the initiator at 60℃ for 2h. The number-averaged molecular weights of copolymers 1a, 1b, and 1c were 14800, 47900, and 13800, respectively. The contents of 4-SDP in copolymers 1a, 1b, and 1c were determined with the integral ratios of signals in ^1H NMR spectra, and were 9,

13, and 22 mol%, respectively (Table 1). In the next synthetic stage, under an inert gas atmosphere, these polymer ligands successfully reacted with [IrCl(COD)(2,2'-biphenylene)]$_2$ in CH_2Cl_2 at ambient temperature for 24h to form an orange precipitate which suggested generation of the iridium-containing bisphosphine polymers, 2a-e, 3a-e, and 4a-j. The quantities of iridium content in metallopolymers 2a-e, 3a-e, and 4a-j were successfully determined by the measurement of the residues in an ignition test, which revealed that 0.06-0.6 mmol of iridium atom per 1 g of these polymers was included (Table 2). This iridium content depends on the used amount of the iridium precursor, [Ir(cod)(biph)Cl]$_2$. In other words, the iridium content can be precisely controlled by using a specific amount of the iridium precursor, though the result suggested that complete consumption of all phosphine ligands in the ligand-containing polymer by [Ir(cod)(biph)Cl]$_2$ is difficult.

Scheme 2 depicts a synthetic procedure for the monophosphine iridium polymer

complexes, 6a-f, 7a-e, 8a-e. The polymer ligands 1d-f, of which the molecular weights are 19300, 25300, and 11900 g mol^{-1} and contents of the comonomer, 4-SDP, were 14, 16, 22 mol%, were used for the formation of 6-8. These polymer ligands also successfully reacted with [Ir(piq)$_2$Cl]$_2$ in CH$_2$Cl$_2$ at ambient temperature to form an orange to red precipitates facily. In contrast to the case of the bisphosphine iridium complexes, the quantities of iridium content in metallopolymers 6a-f, 7a-e, 8a-e were successfully determined by the integral ratios of the ^{31}P NMR resonances assigned as monomer signals (Table 3). The iridium content in these polymers were 0.02 ～ 0.7 mmol of iridium per 1 g, indicating that the iridium content was well consistent with the feeding amount of [Ir(piq)$_2$Cl]$_2$.

The bisphosphine iridium polymer complexes 2-4 were hardly soluble in usual solvents, such as CH$_2$Cl$_2$, CHCl$_3$, toluene, hexane, THF, 1,4-dioxane, ethyl acetate, acetone, acetonitrile, and methanol, because two phosphine units in two independent polymer ligands coordinating one iridium center should result in cross-linking

of the polymers. However, in CD$_2$Cl$_2$, signals due to a metal-containing polymer, which was obtained by the reaction of 1b with [Ir(cod)(biph)Cl]$_2$, were successfully detected in the ^{31}P NMR spectrum. Figure 5 (a-c) show the ^{31}P NMR spectra of complex 5a (R = H), polymer ligand 1b, and metallopolymer 3c (used polymer ligand 1b, Ir/P =0.19), respectively. The signal due to the phosphorus of the tertiary phosphine was observed at δ -5.3 (b), whereas new resonance due to 3c appeared at δ 21.9 (c). This signal in the spectra of 3c, of which the chemical shift was similar to that at δ 22.5 (a) in the non-polymer analogue 5a, suggested the generation of new iridium-phosphorus bonds in the metal-containing polymers.

In sharp contrast to the insolubility of 2-4, the monophosphine iridium polymer complexes 6-8 were readily soluble in several organic solvents, such as CH$_2$Cl$_2$, and CHCl$_3$, indicating no cross-linking structure exists in these metallopolymers. Thus, ^{1}H and ^{31}P NMR measurements of the series of the synthesized compounds were conducted as shown in Figure 6(a-d) and Figure
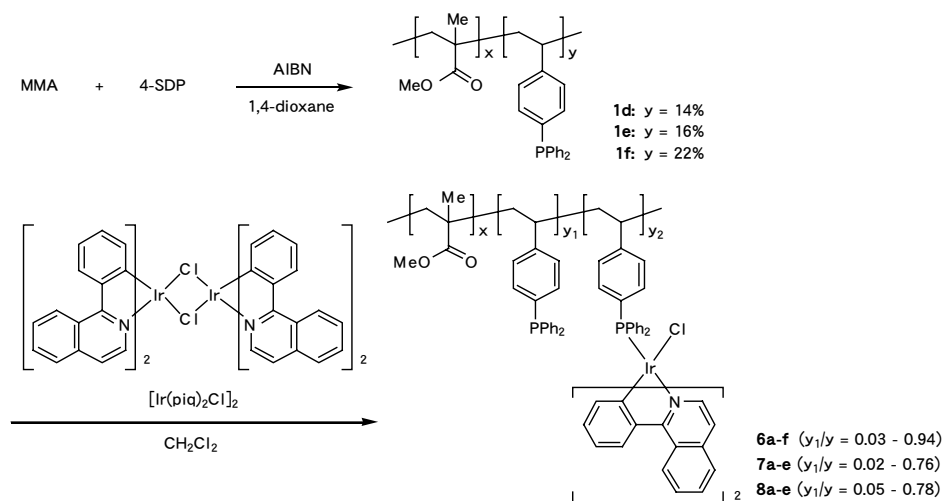
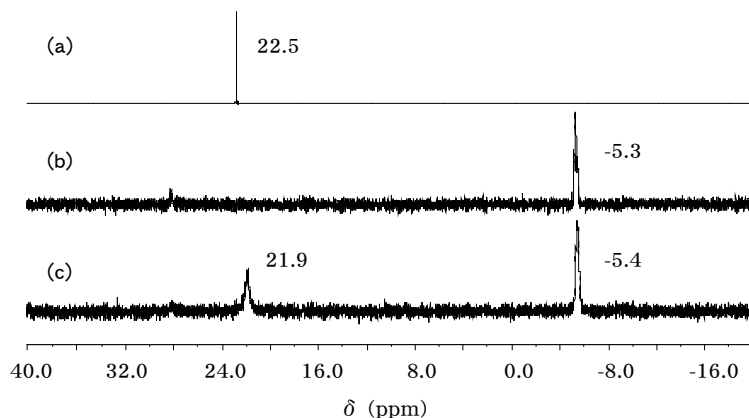Scheme 2.　Preparation of metal-containing polymer 6a-f, 7a-e, 8a-e.

Figure 5. ^{31}P NMR spectra for (a) compound 5a, (b) polymer ligand 1b, and (c) metallopolymer 3c.

7(a-d). The ^{1}H NMR spectra for the non-polymer iridium complex 9 [Figure 6 (a)], the polymer ligand 1d [Figure 6 (b)], and metallopolymers, 6e [Figure 6 (c)] (used polymer ligand 1d, Ir/P = 0.62), and 6f [Figure 6 (d)] (used polymer ligand 1d, Ir/P = 0.94). The signal due to aromatic protons of the polymer ligand appeared at from δ 6.6 to 7.8, whereas broader new resonances were observed from δ 9.3 to 6.1, assigned as aromatic protons of the incorporated iridium unit [Figure 6 (c, d)] which are similar to those corresponding to the non-polymer complex 9 [Figure 6 (a)]. In the ^{31}P NMR spectra [Figure 7(a-d)], the incorporation of iridium unit can be confirmed by the observation of the new signal at δ -2.9 to -1.8 due to the iridium-bound phosphorus atom of the metallopolymers 6e and 6f [Figure 7(c, d)]. This signal did not appeared in the spectrum for the polymer ligand 1d [Figure 7(b)] and was almost the same as that for the non-polymer iridium complex (δ -1.45) [Figure 7(a)]. This result suggested that the incorporated iridium unit in the polymer has the same chemical structure as that of the non-polymer iridium complex 9. Unfortunately, phosphine pendant groups without the iridium unit in

these polymers 6-8 were easily oxidized to form phosphine oxides during the usual experimental operations [Figure 7(c)].

3-2. Photoluminescence Behavior of Iridium Complexes

Since the metallopolymers were hardly soluble, the excitation and emission spectra were measured in the solid state with an attachment for solid-state measurement. The shape of spectra for all of the bisphosphine iridium polymer complexes, 2a-e, 3a-e, and 4a-j, resembled those measured in non-polymer analogues 5a-f.

The excitation and emission spectra for metallopolymer 3c and the emission spectra for 5a (R = H) and 3c (used polymer ligand 1b, Ir/P = 0.19) are shown in Figure 8, (a, b), respectively.

In Figure 8 (b), the wavelength at the maximum intensity of 3c was 597 nm, which was 21 nm shorter in comparison with that of 5a. This blue shift did not rely on the iridium content, the MMA/4-SDP ratio, or the molecular weight in polymer ligands 1a-c at all. On the other hand, according to a calculation of the density of the iridium unit in the metallopolymer, the ratio of photoluminescent intensity of 3c to
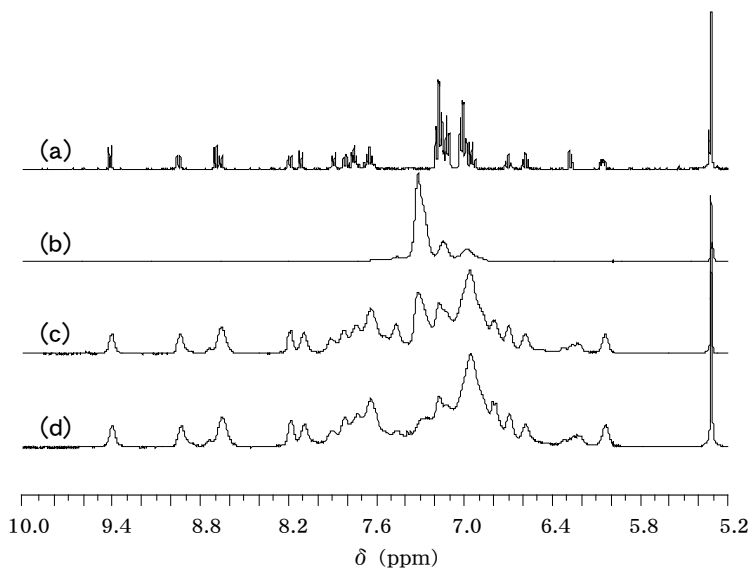
Figure 6. ^{1}H NMR spectra for (a) compound 9, (b) polymer ligand 1d, and (c) metallopolymer 6e, and (d) metallopolymer 6f.
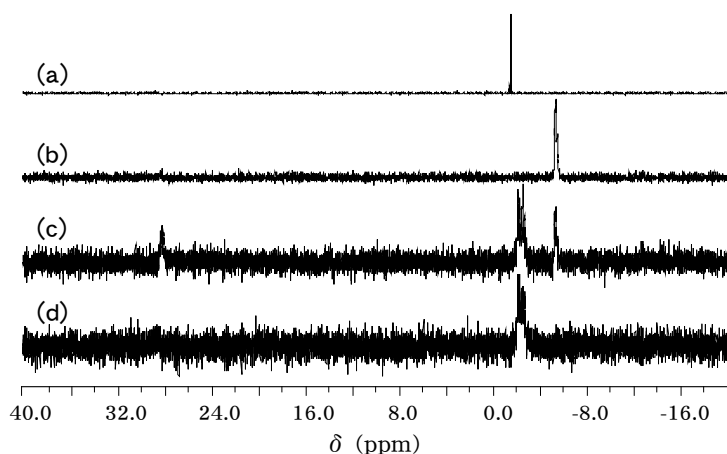

Figure 7. ^{31}P NMR spectra for (a) compound 9, (b) polymer ligand 1d, and (c) metallopolymer 6e, and (d) metallopolymer 6f.

that of 5a should be 17% when their quantum yields of luminescence are assumed to be the same, however, the measured intensity of 4c was lower (9%).

Because the iridium unit in the iridium-containing polymer is regarded as one of the analogues bearing (4'-alkylphenyl)diphenylphosphine ligands, the luminescence properties of several small iridium analogues having 4'-substituted phenyldiphenylphosphines (5b: R = Me, 5c: R = NMe$_2$, 5d: R = CH = CH$_2$, 5e: R = Ph, 5f: R = CO$_2$H) (Figure 4) were investigated. These analogues 5b-f were prepared in a way similar to that of 5a in 18-72% yields and were characterized using standard spectral techniques. The results of PL spectral studies of complexes 5a-f in the solid state are shown
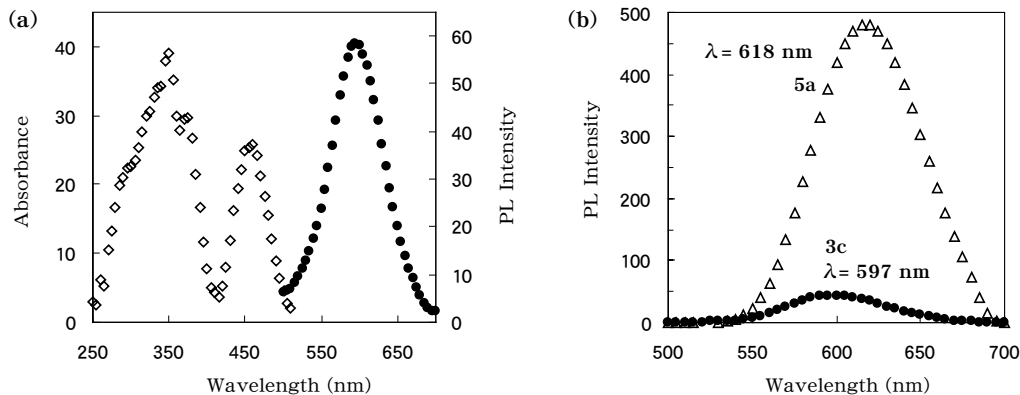
Figure 8. Powder-state excitation◇ and emission● spectra for metallopolymer 3c are shown in part (a) and emission spectra for 5a and 3c are shown in part (b).

in Figure 4. In all spectra for 5b-f, the blue shift from that for 5a was observed, and the substituents were revealed to make an obviously lower intensity of luminescence. This is probably due to radiationless deactivation as a consequence of binding huge substituents, the polymer main chain, to the phosphines in each iridium unit. Reportedly, studies on luminescent anthracene analogs bearing a large polyamine dendrimer demonstrated deactivation similar to our case.[20]
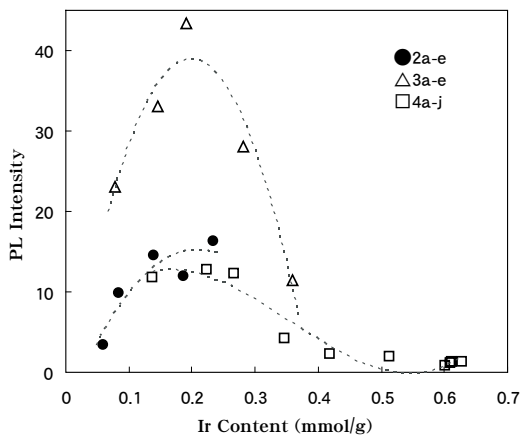

Figure 9. PL intensity *versus* Ir content for the metallopolymers. Symbols indicate the metallopolymers: ●, 2a-e; △, 3a-e; □, 4a-j.

Further, it is of interest that the intensity of metallopolymers 2a-e (used polymer ligand 1a, $M_n =14800$), 3a-e (used polymer ligand 1b, $M_n =47900$), 4a-j (used polymer ligand 1c, $M_n =13800$) increased and then decreased with an increase in the iridium content (Figure 9). As the iridium content increased up to 0.2 mmol/g of the polymer, the intensity also increased, but more Ir content above that point induced a decrease in the intensity.

The decrease in the intensity at a high Ir content level may be due to self-quenching. In most luminescent iridium materials, the strongest intensity has been observed at the lowest concentration due to the vanishing of the self-quenching mechanism.[21] Moreover, we compared luminescence properties among cross-linked metallopolymers 2-4 having different molecular weights synthesized via *Method B*, since the molecular weight of a polymer ligand from radical copolymerization of 4-SDP and MMA could be controlled easily, whereas those among known metallopolymers prepared by *Method A* were not compared. The luminescent intensities of 3a-e were stronger than those of 2a-e and 4a-j, for which the molecular weight of the ligand-containing

polymers 1a and 1c was smaller than that of 1b. In principle, no correlation between intensity and molecular weight of usual luminescent metallopolymers should be observed and have not been reported to our knowledge. This result explains a specific character of the cross-linked metal-containing polymers, maybe due to the rigidity of the structure of cross-linked polymers changed by the number of linking points in one polymer, which might restrain the radiationless deactivation process. We noticed that the amount of the Ir content was consistent with a number of a cross-linking point in a metallopolymer made by the coordination of two phosphines at different points on one iridium center. Thus, probably, the emitting intensity of the metallopolymer strongly depends on the rigidity of the structure due to cross-linking. That is, when these polymers are highly cross-linked, radiationless deactivation may not be induced by the rigid surrounding structure of the emitting iridium center, whereas a more flexible structure of the metallopolymer enables facile radiationless deactivation at a low Ir content level.

In addition, we have to discuss whether the number of free phosphine ligands in an iridium-containing polymer prepared via *Method B* influences the properties of the photoluminescence. In order to compare them, we chose two sets of metallopolymers, 2c-e and 4a-b, both of which have similar iridium content, 0.14-0.23 and 0.14-0.22, but contain a different amount of phosphorus, Ir/P $=0.19$-0.32 and 0.09-0.15, respectively (Table 2). As a result, the luminescent intensities and wavelengths have little difference between the two sets (Figure 9), suggesting that free phosphine ligands in an iridium-containing polymer do not affect the photoluminescence.

We next measured PL spectra for mo-nophosphine iridium polymer complexes 6a-f, 7a-e, 8a-e. The emission wavelength of these metallopolymers did not depend upon the iridium content in the polymers, the 4-SDP/MMA ratios in the copolymer ligands, and the molecular weight of the polymers, exhibiting similar emission spectra at the same region. As the typical example, emission behavior of metallopolymer 6e (used polymer ligand 1d, Ir/P $=0.94$) were compared with that of non-polymer complex 9 in both the solution (0.1 g/L) [Figure 10 (b)] and solid states [Figure 10 (a)].

In the solid state, PL spectrum for metallopolymer 6e illustrated simple monomodal absorbance at 614 nm, whereas that for non-polymer complex 9 showed large absorbance at 607 nm and small shoulder around 635 nm. Further, the PL intensity of 6e was definitely higher than that of 9 [Figure 10(a)]. This advantage may be caused by dilution effect of the emitting moiety because of the existence of the large polymer back bone in 6e. In the solution state, unlikely both compounds showed similar emission signals at 600 nm [Figure 10(b)]. It is interest that the PL results of 6e and 9 demonstrated the same emission intensity in Figure 10 (b), because the iridium-unit concentrations in the solutions of 6e and 9 differed from each other, 0.48 and 1.1 mmol/g, respectively. This indicates higher quantum efficiency of 6e than that of 9 essentially.

Plots between the iridium content of 6a-f (used polymer ligand 1d, $M_n=19300$), 7a-e (used polymer ligand 1e, $M_n=25300$), and 8a-e (used polymer ligand 1f, $M_n=11900$) vs. their emission intensity was shown in Figure 11. As is similar to the bisphosphine iridium polymer complexes 2a-e, 3a-e, and 4a-j, the highest emission intensity for the monophosphine iridium polymer complex-
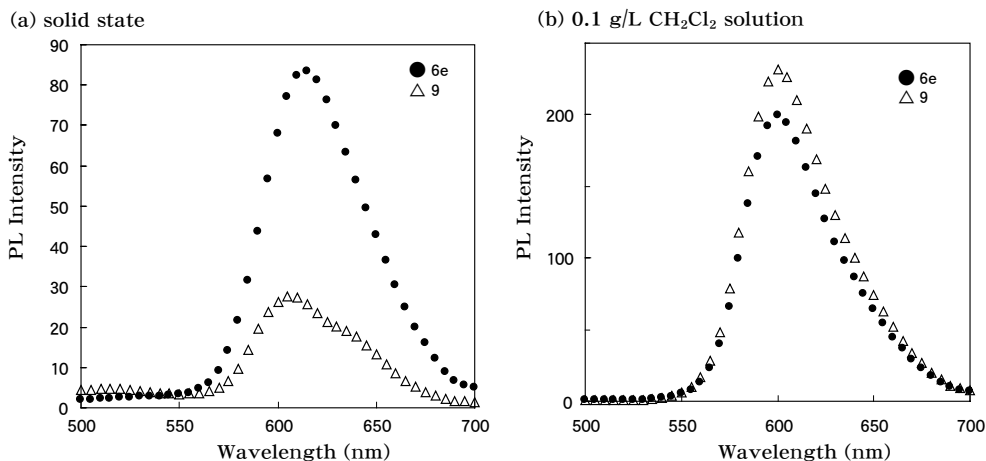
(a) solid state

(b) 0.1 g/L CH$_2$Cl$_2$ solution

Figure 10. Solid-state emission spectra for 9 and metallopolymer 6e are shown in part (a) and solution-state emission spectra for 9 and 6e are shown in part (b).

es 6a-f, 7a-e, and 8a-e did not rely on the 4-SDP/MMA ratios of the polymer ligand precursors 1d-f, but increased with gaining the iridium content in the polymers and then decreased with the iridium content over 0.5 mmol/g.
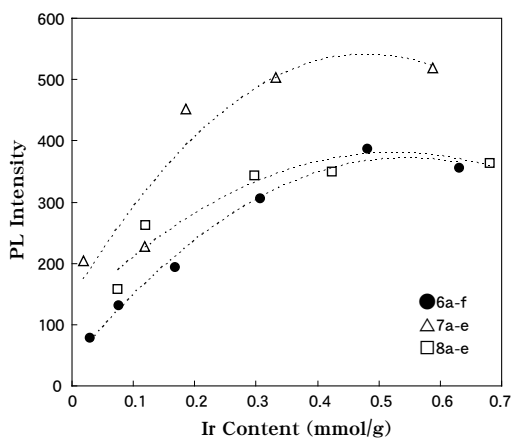
Figure 11. PL intensity *versus* Ir content for the metallopolymers. Symbols indicate the metallopolymers: ●, 6a-f; △, 7a-e; □, 8a-e.

This diminution of the intensity with high iridium content was also attributable to the self-quenching mechanism as is observed with bisphosphine polymer com-

plexes 2-4 (Figure 9). However, relationship between the molecular weight of the polymer ligand precursors and the emission intensity for 6-8, which was clearly pointed out in metallopolymers 2-4, was not detected, suggesting the specificity of metallopolymers 2-4 owing to their cross-linking structures.

4．SUMMARY

Consequently, we successfully prepared two types of cyclometallated-iridium-containing metallopolymers, where the iridium unit binds to MMA/4-styryldiphenylphosphine (4-SDP) copolymer with phosphine-ligand pendant. The synthetic method of these polymers via the reaction of polymer ligands with iridium complex precursors is applicable in incorporation of many types of luminescence units into the polymer chain and is favorable in investigating the chemical relationships between the luminescent behavior and their structures. NMR analysis revealed that the iridium units in the metallopolymers has the same structural features as that of the corresponding

non-polymer complexes.

The cross-linking structure of the bisphosphine polymer complex resulted in showing different chemical and luminescent properties from those of the non-cross-linking monophosphine polymer complex. The former cross-linking polymer is hardly soluble in various solvents, whereas the latter is soluble in organic solvents. The luminescence behavior of the former is obviously different from the corresponding non-polymer bisphosphine complex, though that of the latter is similar to that of the non-polymer monophosphine complex, which can be regarded as the proper luminescence model compound of the corresponding metallopolymer. Interestingly the emission intensity of the former polymer clearly relied on the molecular weight of its polymer ligand precursor, even when the iridium content did not change. This luminescence nature may be specific in these cross-linking metallopolymers. Therefore, significance of the cross-linking luminescent polymers can be pointed out especially in an application of interfacial-diffusion-restrained[22] emitting devices required in multilayer PLED. Now we are researching other ligand copolymers with host ability or charge-transporting ability instead of insulated MMA, and other anchor ligands than phosphines.

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