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Review

Metal containing polymers with heterocyclic rigid main chains

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Contents

Abstract

This paper provides an overview on some metal containing polymers that contain heterocyclic systems and metal complexes on the main chain. Heterocycles such as 1,3,4-oxadiazoles, quinoxaline, dipyridophenazine, and benzimidazole may enhance the electron carrier mobilities of the polymers, while the incorporation of ruthenium or rhenium diimine complexes to a conjugated polymer may change the photophysical properties of the resulting polymers significantly. The heterocyclic conjugated main chain can be constructed by condensation ring closure or metal catalyzed coupling reactions. Polymers that contain bidentate or tridentate ligands on the main chain were used for metal coordination. These metal containing polymers have found potential applications in organic opto-electronic devices such as light emitting diodes, optical detectors, and photovoltaic cells. Some metal containing rigid rod polymers based on non-conjugated main chain will also be presented. Metal containing polyimides, polyamides, and polyesters exhibit good thermal stability due to the rigid main chain. Some of them also exhibit thermotropic and lyotropic liquid crystal properties. The effect of incorporating metal complex to the physical properties of the polymers was investigated.

Keywords: Metal complexes; Conjugated polymers; Heterocycles; Opto-electronics

1. Introduction

In the first example of metal containing polymers reported by Arimato et al., vinyl ferrocene and other vinylic transition metal π-complexes were polymerized under the same conditions as conventional organic olefinic monomers to yield high molecular weight polymers [1]. Since then, the field of metal containing polymers has been gaining more attention because of their potential important applications. By incorporating metal complexes into a polymer molecule, the physical and chemical properties of the resulting material may be modified by the metal complexes present, while the film forming properties exhibited by the polymer can be retained. Metal containing polymers have been applied in different areas of research such as polymer catalysts [2,3], metallomesogens [4], supramolecular metal complexes [5], dendritic polymers [6], and in the construction of supramolecular systems [7], etc. In general, metal complex moieties can be attached to the polymer molecule as

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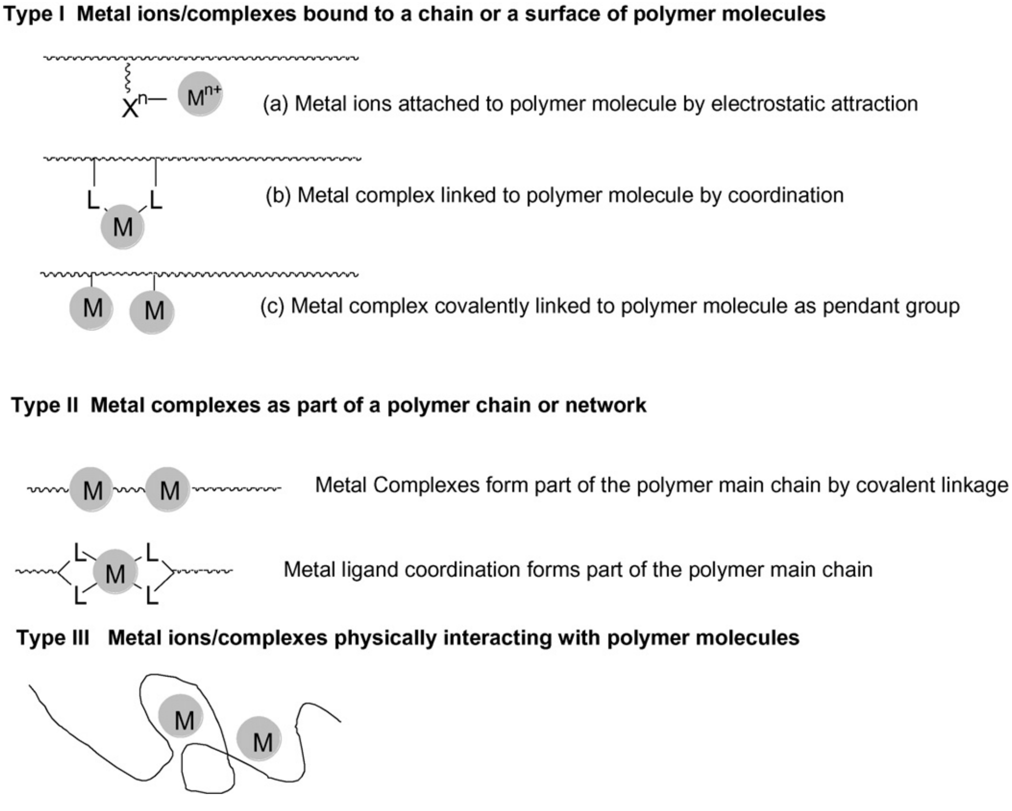

Fig. 1. Different approaches in synthesizing metal containing polymers.

part of the main chain or pendant groups. According to the classification by Ciardelli et al., there are three different types of metal containing polymers (Fig. 1) [8]. In Type I polymers, the metal ions/complexes are attached to the polymer molecule at the side chain or end group by electrostatic interaction, coordination bond, or covalent bonding. In Type II polymers, the metal complexes constitute part of the polymer main chain by metal–ligand coordination or covalent linkage. In Type III polymers, the metal ions embed in the polymer matrix by physical interaction. The driving force for the formation of these polymers is the negative free energy as a result of the polymer chelate effect.

Research studies in the syntheses and properties of metal containing polymers have been summarized in several reviews [9–21]. Our continuous research effort has been focused on the synthesis of multifunctional metal containing polymers in which the polymer main chain and the metal complexes could perform different functions. For example, when a metal complex with strong absorption in the visible region is attached to a conjugated polymer main chain, the photosensitivity of the resulting polymer in this region will be enhanced. In addition, when the complexes were excited by light irradiation, the excitons formed would be separated and transported by the conducting conjugated polymer main chain. Such polymers have potential applications in photovoltaic devices. An example of these metal containing conjugated polymers is shown in Fig. 2. The polymer was synthesized by the palladium catalyzed coupling reaction between 1,4-divinylbenzene and the dibromo-substituted bisterpyridyl ruthenium(II) complex [22]. The metal complex content in polymer **1** can be conveniently tuned by changing the monomer ratio in the polymerization reaction. The ruthenium complex can enhance the photosensitivity of the polymer beyond 500 nm at which the polymer main chain does not absorb [23]. In addition, the photocurrent current response and charge carrier mobilities of the polymer are depending on the metal content [24], which strongly indicates the metal complexes are playing important roles in the photo charge generation and charge transport process.

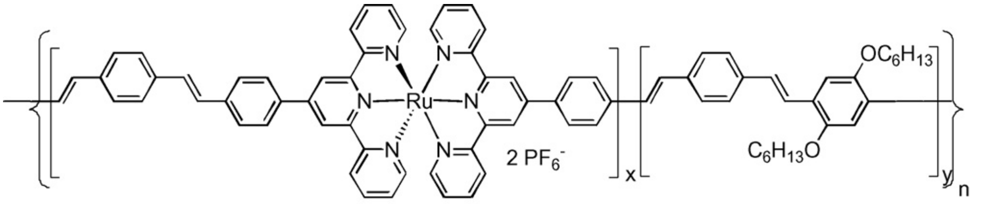

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Fig. 2. An example of conjugated poly(*p*-phenylenevinylene) with bis(2,2′:6′,2″-terpyridine) ruthenium(II) complex on the main chain.

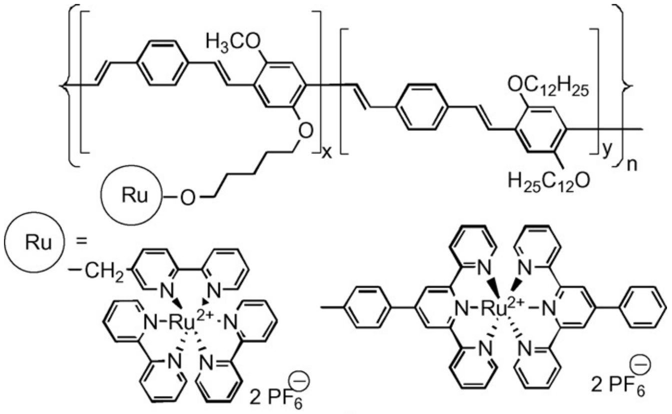

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Fig. 3. Poly(*p*-phenylenevinylene)s incorporated with different ruthenium complexes as pendant groups.

When an emissive metal complex is incorporated into a luminescent conjugated polymer main chain, both the complex and polymer may function as light emitter. Fig. 3 shows a series of poly(*p*-phenylenevinylene) **2** with pendant ruthenium bipyridine or terpyridine complexes. The UV–vis absorption spectra of the polymers show intense absorption bands due to both the conjugated main chain and the ruthenium complexes [25]. However, their photoluminescence spectra are dependent on the metal complex content. When the polymer contains 10% ruthenium bipyridine complex per repeating unit, emissions from both main chain and complex can be observed. However, when the ruthenium complex content is increased to 20%, the emission from the main chain is partially quenched by the ruthenium complex, which has lower-lying metal-to-ligand charge transfer (MLCT, d–π*) excited states than the π–π* excited state of the main chain.

Besides conjugated main chains based on carbon atoms, other heterocyclic systems may also be used in the construction of organic conjugated polymers. Introduction of heteroatoms (e.g. nitrogen) to the conjugated main chain may result in a significant change in the energy level of the polymer. This paper gives an overview on some metal containing polymers with heterocyclic main chain. Discussion will be focused on the influence of the heterocyclic units/metal complex to the optical and electronic properties of the polymers. Some heterocyclic units form very rigid conjugated system, resulting in the enhancement in the thermal stability of the polymer. The second part of the paper describes the synthesis and properties of some metal containing polymers with non-conjugated rigid main chain. The syntheses, applications, and the effect of incorporating metal complexes to the physical and chemical properties of the polymers will be presented.

2. Metal containing conjugated polymers

2.1. Conjugated polymers with 2,2′-bipyridine moieties on the main chain

2,2′-Bipyridine (bpy) is a highly versatile bidentate ligand for a variety of metal ions. The application of this ligand in a variety of molecular and polymeric materials has

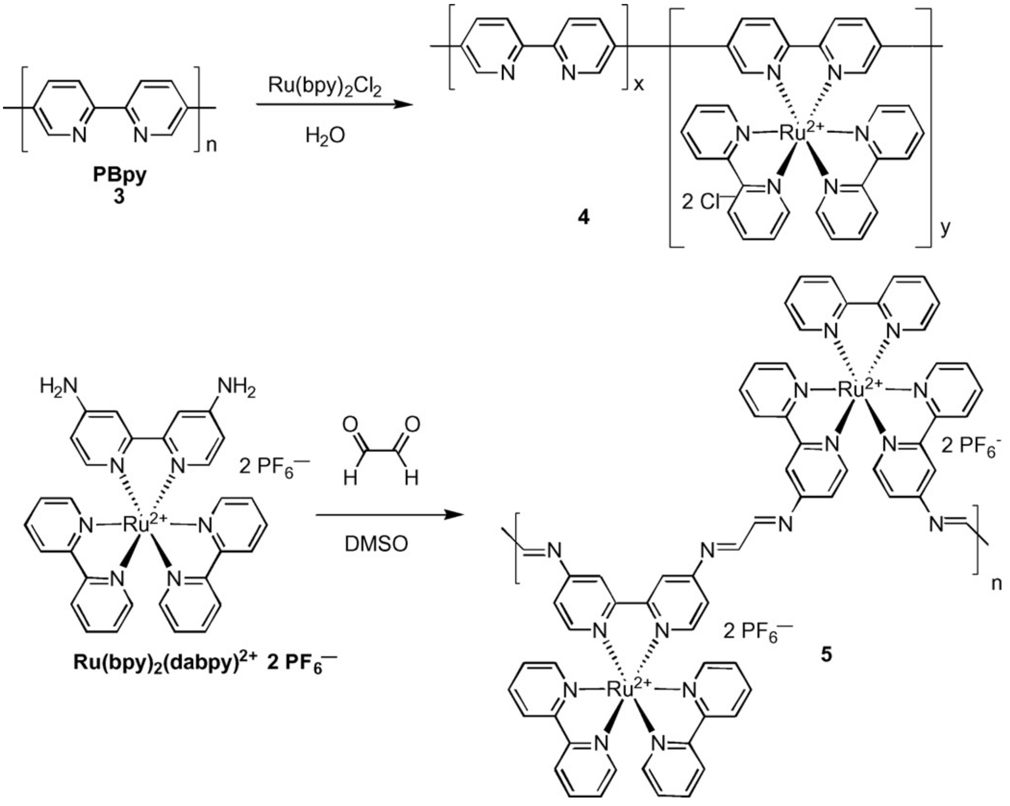
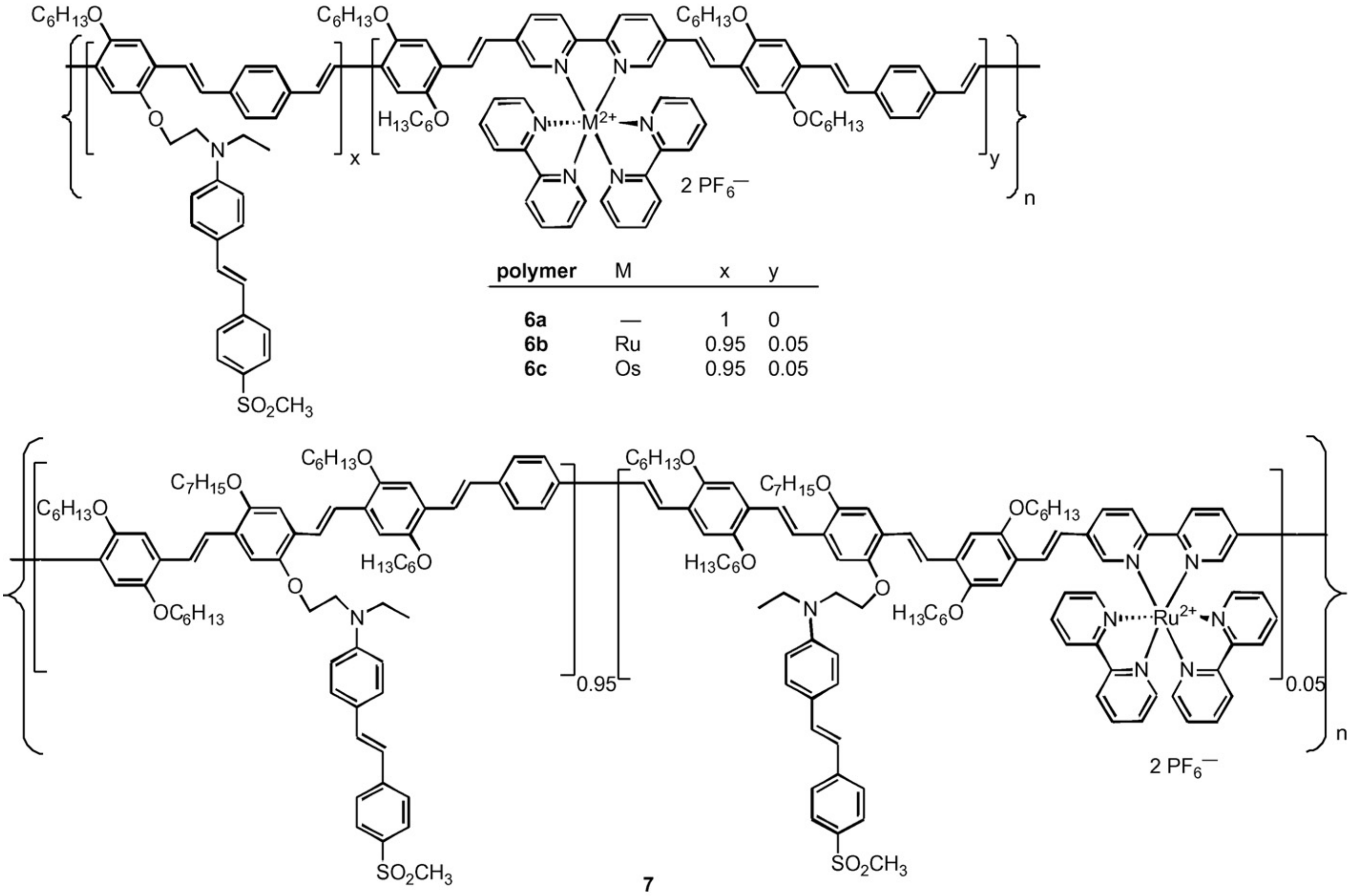


Fig. 4. Synthesis of conjugated polymers **4** and **5** with 2,2′-bipyridyl moieties on the main chain.

been demonstrated [26]. Most of the ruthenium containing conjugated polymers reported in the literature are based on 2,2′-bipyridine as the ligand. In 1992, Yamamoto et al. report the synthesis of poly(2,2′-bipyridine-5,5′-diyl) (**3**) by the reductive coupling of 5,5′-dibromo-2,2′-bipyridine with $Ni(cod)_2$ (cod = cyclooctadiene) [27]. Polymer ruthenium complex **4** was synthesized by the reaction between **3** and $[Ru(bpy)_2Cl_2]$ in water under reflux [28] (Fig. 4). Approximately 1.3% of the bipyridine units were functionalized with Ruthenium complex. When the metal free polymer was *n*-doped with sodium naphthalide, it exhibited an electrical conductivity of $1.6 \times 10^{-1}\,S\,cm^{-1}$ [29], which clearly demonstrated the electron deficiency of the pyridine moieties on the main chain. There was electron exchange between the coordinated ruthenium species, which may occur through the π-conjugation system of the conjugated polymer ligand. 2,2′-Bipyridine containing conjugated polymer **5** based on the imine linkage can be constructed by the condensation reaction between $Ru(bpy)_2(dabpy)^{2+}$ (dabpy = 4,4′-diamino-2,2′-bipyridine) and glyoxal [30]. The resulting polymer, which is soluble in polar solvents such as DMF and DMSO, exhibited a short-lived excited state and weaker emission when compared to $Ru(bpy)_3{}^{2+}$, attributed to the lower intersystem crossing efficiency from the ^{1}[MLCT] to the emissive ^{3}[MLCT] states.

The $Ru(bpy)_3{}^{2+}$ moieties can also be used to enhance the photosensitivity in the visible region within which the conjugated main chain does not absorb. Yu et al. reported the synthesis of a series of $Ru(bpy)_3{}^{2+}$ containing conjugated polymers incorporated with second order nonlinear optical chromophores (Fig. 5). The polymers showed an enhancement in photoconductivity owing to the enhancement in photoinduced charge separation by the ruthenium complexes [31]. Later, the use of $Ru(bpy)_3{}^{2+}$ as the photosensitizers in multifunctional polymers with second order nonlinear optical properties was reported [32]. Polymers **6a–c** that contain $Ru(bpy)_3{}^{2+}$ or $Os(bpy)_3{}^{2+}$ moieties on the main chain and a donor–acceptor type stilbene derivative acted as the nonlinear optical chromophore. The polymers exhibited the photorefractive effect, which is the modulation of the refractive index of a material by a space charge field via the electro-optic effect. The space charge field is generated due to the charge redistribution resulting from irradiation of two coherent laser beams [33]. Therefore, the choice of a suitable photosensitizer is very important. Compared to the metal-free polymer **6a**, the ruthenium containing polymer **6b** exhibited higher photoconductivity at 690 nm due to the enhancement in absorption by the ruthenium complex. The photorefractive effect was studied by the two beam coupling experiment, and polymer **6b** showed a higher optical gain (300 cm^{-1}). Polymer **6c**, which contained osmium complex as the photosensitizer, showed an absorption tail extending beyond 600 nm. Although its optical gain was measured to be 80 cm^{-1}, the photorefractive response in the near IR region is very interesting. This type of



polymer	M	x	y
6a	—	1	0
6b	Ru	0.95	0.05
6c	Os	0.95	0.05

7

Fig. 5. Ruthenium and osmium containing conjugated polymers **6–7** for photorefractive applications.

metal containing conjugated polymers can also be synthesized by the metal coordination of the metal free polymer, which were obtained by the Homer–Wadsworth–Emmons reaction instead of the Heck reaction. For example, polymer **7** was synthesized by the reaction between the metal free polymer and $Ru(bpy)_2Cl_2$ in THF. The polymer exhibited higher solubility in organic solvents such as THF and chloroform. The optical gain was measured to be 99 cm^{-1}. The photorefractive performance of the polymers was limited by the internal electric field generated by the ion pairs, which resulted from the applied external field in the chromophore alignment process [34]. When the external electric field was increased from 10 to 50 V/μm, the optical gain increased from ca. 5 to 25 cm^{-1}. Further increase in electric field strength gave no increase in optical gain. At the field of 80 V/μm, an optical gain of 26.6 cm^{-1} was measured. The dynamics of the formation of optical grating were studied by the degenerate four-wave mixing experiments. The time dependent diffraction intensity can be fitted by a biexponential function. In general, a fast initial rise in the diffraction signal was observed, which was followed by a slow writing period for approximately 5 s.

Guillerez et al. demonstrated the synthesis of a ruthenium containing conjugated polymer **11** (Fig. 6) consisted of alternating units of regio regular quarter(3-octylthiophene) and 2,2′-bipyridine units [35]. Metalation of the metal free conjugated polymer **8** with $Ru(bpy)_2Cl_2$ in refluxing ethanol gave unsatisfactory results, and the investigation of the polymerization reaction was focused on the reaction between stannylated quarter(3-octylthiophene) (**9**) and dibromo substituted ruthenium complex **10**. Polymer **11** exhibited three oxidation and four reduction processes as observed in cyclic voltammetry experiments. The first two oxidation processes at +0.65 and +0.78 V (versus Ag/Ag^+ reference electrode) were assigned to the oxidations of the π-conjugated polymer main chain. The third oxidation wave at +1.05 V was assigned to the oxidation at the ruthenium center. For the reduction processes, the first two waves at −1.3 and −1.55 V were well resolved and the last two waves at ca. −2 V were poorly resolved. The first reduction peak was assigned to the reduction of the bipyridine units on the main chain, while the second and third peaks were assigned to the remaining unsubstituted bipyridine ligands.

Besides ruthenium containing polymers, conjugated polymers incorporated with chlorotricarbonyl 2,2′-bipyridyl rhenium(I) complexes on the polymer main chain were also reported. Like their ruthenium counterparts, rhenium(I) diimine complexes also exhibit long-lived excited states that have the MLCT character as well as several reversible metal and ligand based redox processes. In addition, other electronic transitions such as ligand-to-ligand charge transfer and ligand-to-metal charge transfer are also possible, depending on the energy levels of the ligands [36]. A series of rhenium containing polymers **15a–d** with different metal content were synthesized by the Sonogashira coupling reaction between the rhenium complex of 5,5′-diethynyl-2,2′-bipyridine (**12**), 4,4′-diethynylbiphenyl (**13**), and dialkoxydiiodobenzene (**14**) [37] (Fig. 7). The quantum yield and lifetime of the fluorescence due to the main chain π*–π emission decreased with increase of the rhenium content, which was due to the quenching by the rhenium complex. In another paper, the synthesis of rhenium containing π-conjugated oligomers **16** with defined molecular weights was presented [38]. Similar to the polymeric metal complexes, the metal-free oligomers also featured a strong blue emission [39], which was quenched completely after the incorporation of the rhenium complexes. The metal-oligomers showed a weak, relatively long-lived red emission that was originated from the rhenium complex ^{3}MLCT state.

There have been few examples of metal free bipyridine containing conjugated polymers for electrical conducting and metal ion sensing applications. For example, polymers **17** and **18** were synthesized by the electropolymerization of 5,5′-bis(2″-thienyl)-2,2′-bipyridine and 6,6′-bis(2″-thienyl)-2,2′-bipyridine, respectively (Fig. 8) [40]. These polymers are unstable in their p-doped state, but when they were n-doped electrochemically, the electrical conductivities of polymers **17** and **18** were measured to be (3 and 2) × 10^{-8} S cm^{-1}, respectively. In another example, bpy containing polymers with PPV main chain (polymers **19** and **20**) were synthesized Wittig-type reactions [41], and their detailed photophysical properties were

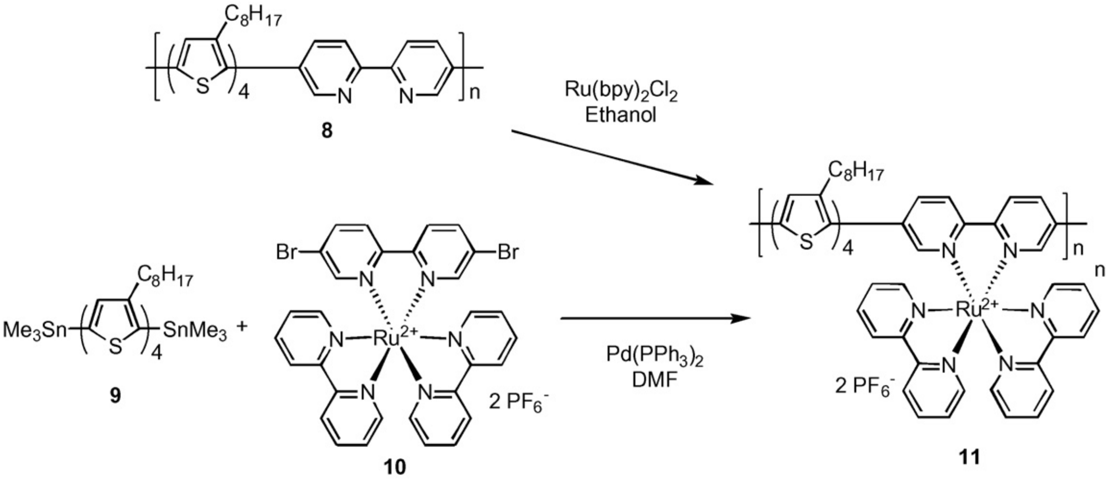
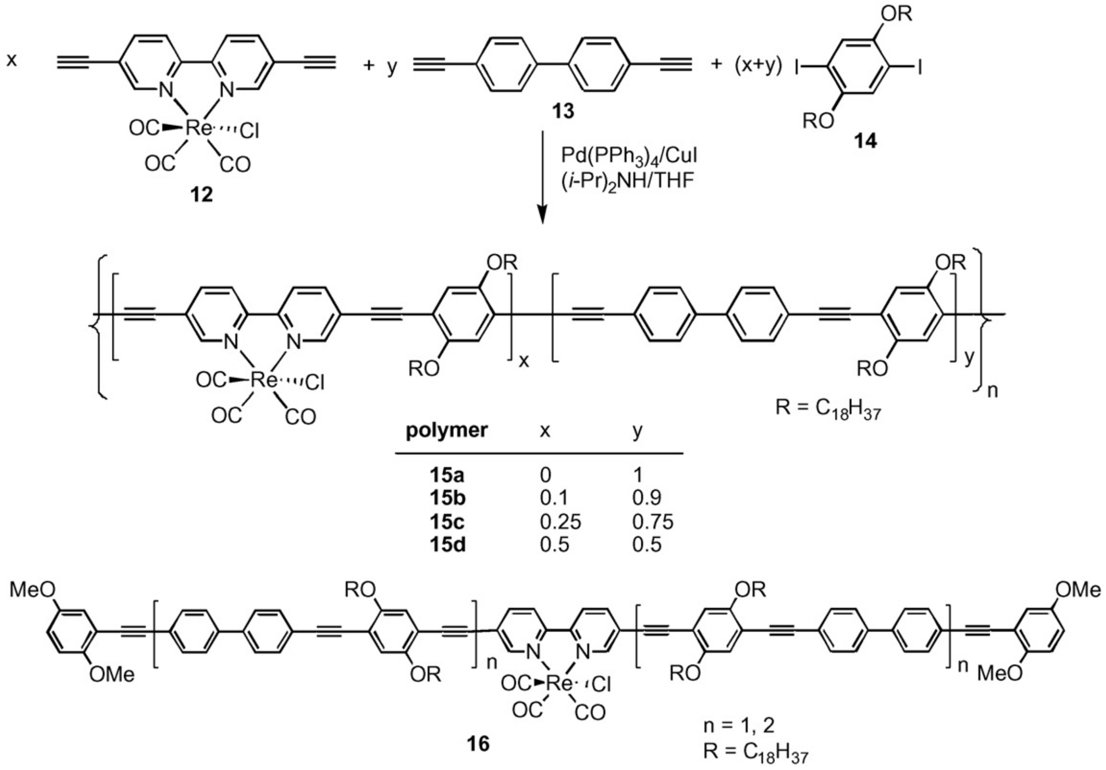


Fig. 6. Synthesis of ruthenium containing polymer **11** with quaterthiophene moieties on the main chain.



polymer	x	y
15a	0	1
15b	0.1	0.9
15c	0.25	0.75
15d	0.5	0.5

Fig. 7. Synthesis of rhenium containing conjugated polymers **15**–**16** using the Sonogashira reaction.

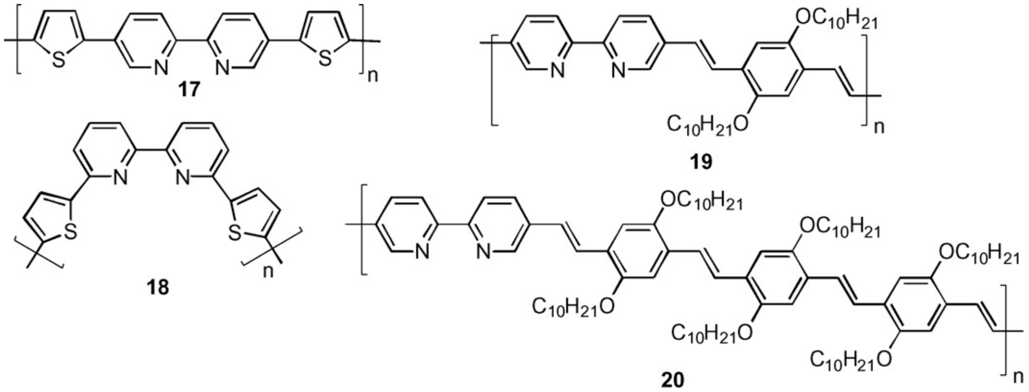


Fig. 8. Metal free bipyridine containing conjugated polymers for metal ion sensing applications.

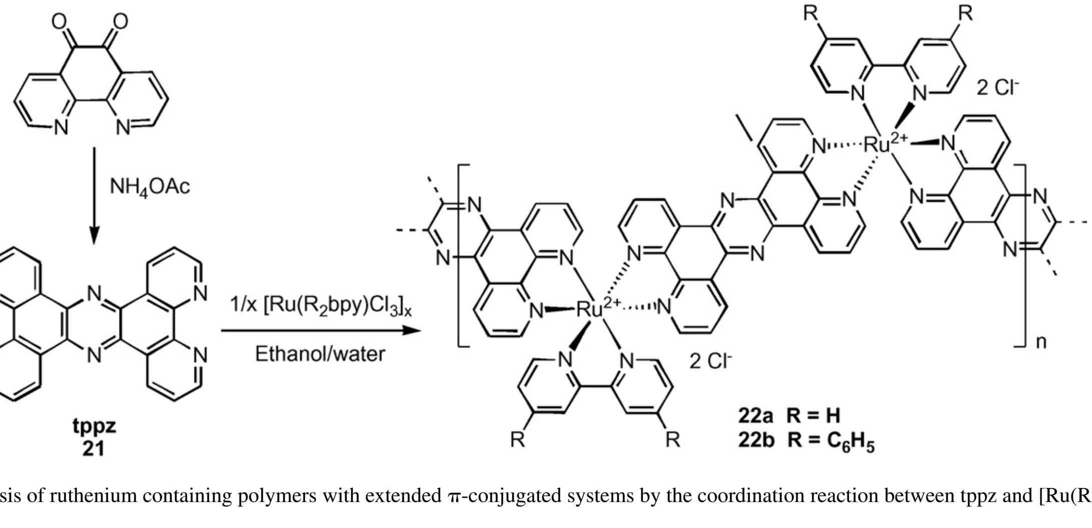
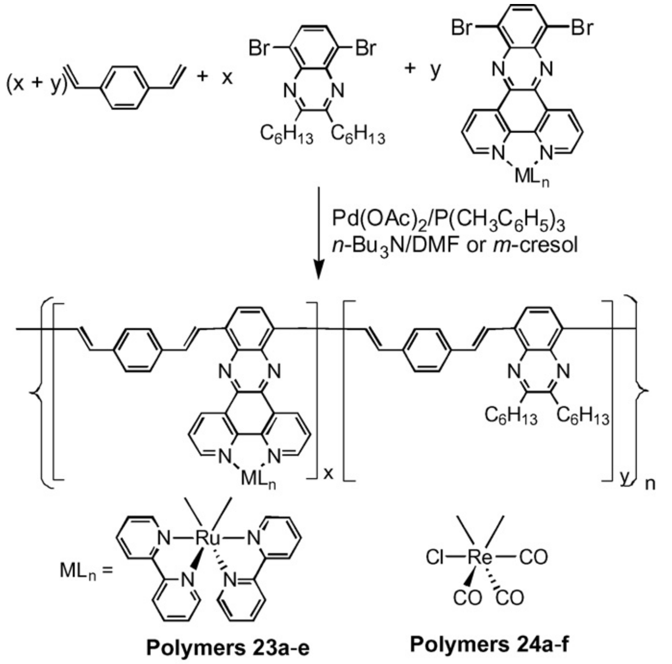


Fig. 9. Synthesis of ruthenium containing polymers with extended π-conjugated systems by the coordination reaction between tppz and $[Ru(R_2bpy)Cl_3]_x$.

reported later [42]. The polymers exhibited ionochromic effects in which the color of the polymer solutions changed instantly upon addition of metal salts. The polymer–metal salt solutions revealed different colors, depending on the metal ions and polymers. The most notable color change in polymer **19** was observed by the addition of Pd^{2+} in which the absorption peak maximum shifted by 109 nm (from 455 to 564 nm). However, some metal ions (Pb^{2+}, Fe^{2+} Fe^{3+}, Cu^{+}, Sb^{3+}, and lanthanides) could quench the fluorescence of the polymers substantially. For another group of metal ions (Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+}, Al^{3+}), they mainly caused a red shift of the emission peak but did not quench the emissions. These phenomena were attributed to different coordination interactions between the bpy units and metal ions. If the meal ions interact with the bpy units in a monodentate fashion, the repulsion between the coordinated metal ions will lead to the twisted conformation between the pyridine rings. On the other hand, those metal ions which formed bidentate complexes with bpy will lead to the planar bpy unit with extended conjugation. These polymers have potential applications in highly reversible and selective metal ion sensing.



Polymer	x	y
23a	1	0
23b	0.8	0.2
23c	0.6	0.4
23d	0.5	0.5
23e	0	1
24a	0.9	0.1
24b	0.8	0.2
24c	0.7	0.3
24d	0.5	0.5
24e	0.4	0.6
24f	0	1

Fig. 10. Synthesis of rhenium and ruthenium containing polymers with dipyridophenazine ligand.

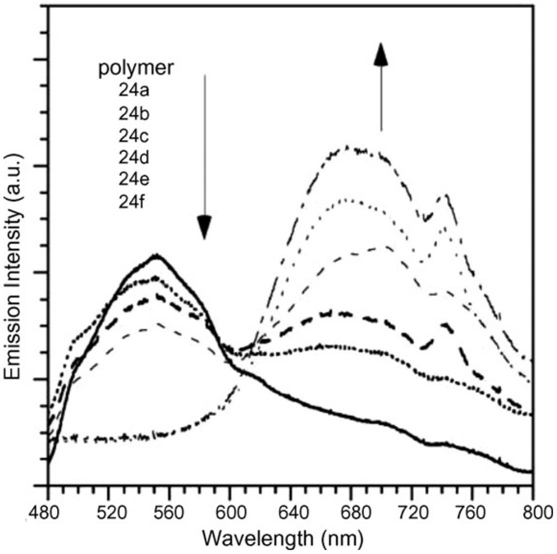


Fig. 11. Photoluminescence spectra of polymers **24a**–**f**. The arrows show the trend of increasing rhenium complex content in the polymers. The figure was reproduced from Ref. [45], with permission from the Royal Society of Chemistry.

2.2. Polymers with quinoxaline/dipyridophenazine units

Besides 2,2′-bipyridine, other bidentate N-donor ligands such as 1,10-phenanthroline and dipyridophenazine were also used in the construction of conjugated polymers. Rehahn et al. demonstrated an efficient method in constructing heterocyclic conjugated systems by the formation of aromatic imine. The heterocyclic ligand tppz **21** with extended π-conjugated ring system was synthesized by treating l,10-phenanthroline-5,6-quinone in a melt of ammonium acetate in 20% yield (Fig. 9) [43]. This ligand can form coordination polymers **22a**–**b** with two different ruthenium complexes, $[Ru(R_2bpy)Cl_3]_x$ (R = H, C_6H_5), by the reaction in water/ethanol mixture [44]. The polymers formed are highly soluble in polar solvents (e.g. dimethylacetamide).

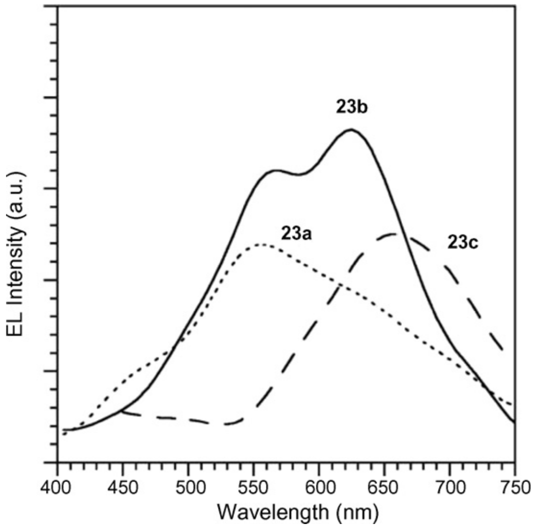
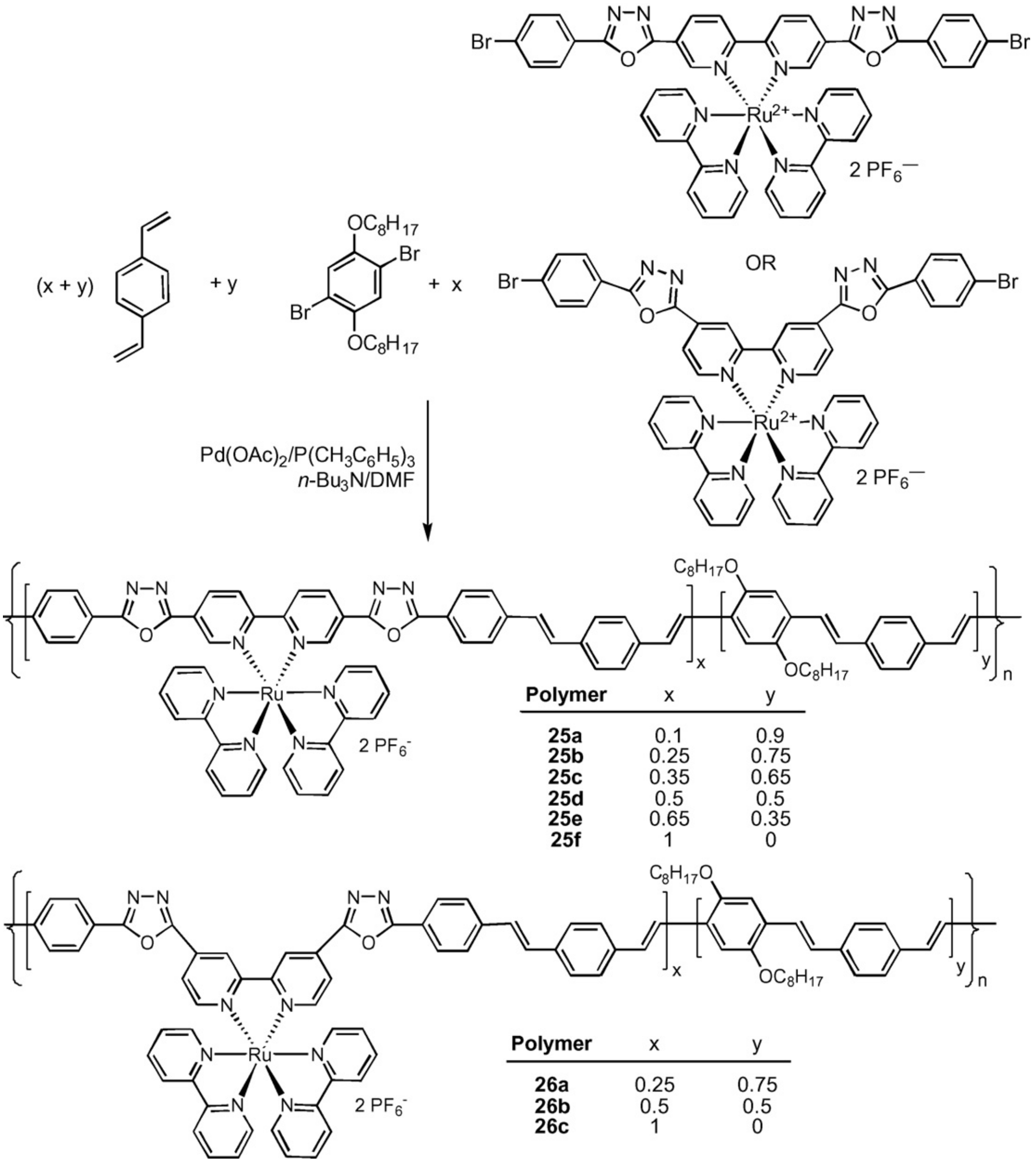


Fig. 12. EL spectra of polymers **23a**, **23d**, and **23e** for the light emitting devices with the structure ITO/polymer/Al. The figure was reproduced from Ref. [45], with permission from the Royal Society of Chemistry.

The highest molecular weight achieved was $M_w \sim 47{,}000$ and the radius of gyration was measured to be 8.4 nm (by light scattering). At low ionic strength, the unsubstituted polymer **22a** (R = H) displayed a more pronounced polyelectrolyte effect than **22b** with substituted phenyl groups (R = Ph). There was a drastic increase in the reduced specific viscosity at decreasing polymer concentration. In the presence of added salt, the polyelectrolyte effect disappeared due to the screening of charges by the ions.

A series of conjugated polymers loaded with ruthenium (polymers **23a**–**e**) or rhenium complexes (**24a**–**f**) based on dipyridophenazine ligand were synthesized by the palladium catalyzed reaction between 1,4-divinylbenzene and the dibromo substituted metal complex monomer [45]. The metal content was varied by changing the ratio of the monomers used (Fig. 10). Dipyridophenazine or quinoxaline are electron deficient units that lower the π* level of the conjugated system [46–48]. These polymers also show two absorption bands at ca. 440 and 550–600 nm, which are due to the absorption by the conjugated main chain and metal complex, respectively. The relative intensities of these absorption bands are dependent on the metal content. The photo luminescence spectra of polymers **24a**–**f** are shown in Fig. 11. When the metal complex content is low, the emission band is dominated by the π*–π emission from the conjugated main chain, and the metal complex emission only appears as a small shoulder. However, when the metal complex content is increased, the lower energy MLCT states may quench the emission from the main chain. Both the hole and electron carrier mobilities increased with the metal complex content. From the time-of-flight experiment, the hole and electron mobilities of polymer **23a** (without metal complex) were (5.5 and 8.5) × 10^{-5} $cm^2V^{-1}cm^{-1}$, respectively. The higher electron carrier mobility indicates the importance



Polymer	x	y
25a	0.1	0.9
25b	0.25	0.75
25c	0.35	0.65
25d	0.5	0.5
25e	0.65	0.35
25f	1	0

Polymer	x	y
26a	0.25	0.75
26b	0.5	0.5
26c	1	0

Fig. 13. Synthesis of conjugated polymers **25**–**26** with oxadiazole moieties on the main chain.

of phenazine for the electron transport process. When the ruthenium complex was increased, both hole and electron carrier mobilities increased ($\mu_h = 3.4 \times 10^{-4}\ \mathrm{cm^2\ V^{-1}\ cm^{-1}}$ and $\mu_e = 4.0 \times 10^{-4}\ \mathrm{cm^2\ V^{-1}\ cm^{-1}}$ for polymer **23e**). The reversible redox process exhibited by the ruthenium center might facilitate the hole transport, while the dipyridophenazine units were responsible for the electron transport process. The ruthenium containing polymers were fabricated into single layer light emitting devices ITO/polymer/Al, and their electroluminescence (EL) spectra are shown in Fig. 12. The EL properties are quite similar to those of the photoluminescence (PL) spectra. Polymer **23d** (with 40% Ru content) shows two emission peaks centered at 550 and 630 nm, while the EL spectrum of polymer **23e** (50% Ru content) is dominated by a single emission peak centered at 660 nm. attributed to energy transfer from the conjugated main to the metal complexes [45].

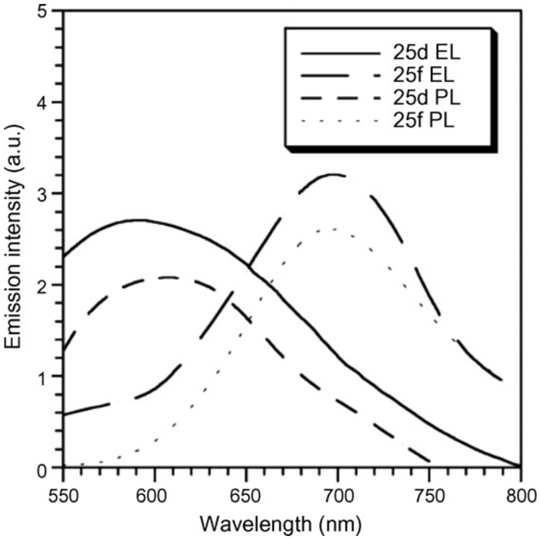


Fig. 14. PL and EL spectra of polymers **25d** and **25f**. The figure was reproduced from Ref. [54], with permission from Wiley-VCH.

2.3. *Oxadiazole containing polymers with high charge carrying mobilities*

In addition to quinoxaline, aromatic 1,3,4-oxadiazoles are also known to be efficient electron transport materials. They were used as the electron transport layer in light emitting devices based on low molecular weight organic molecules [49]. In addition, they can also be incorporated into polymer main chain for the enhancement of electron injection from the cathode so that a balanced charge injections from both cathode and anode can be maintained [50–53]. A series of multifunctional polymers incorporated with both oxadiazole and light emitting ruthenium complex moieties was synthesized by the Heck coupling reaction (Fig. 13) [54]. The oxadiazole units were introduced either at the 5,5′- (for polymers **25a–f**) or 4,4′-positions (for polymers **26a–c**). The ruthenium complex content can be easily controlled by varying the monomer feed ratio during the polymerization reactions. All these polymers exhibited two absorption bands due to the π–π* transition of the conjugated main chain and the d–π* MLCT transition of the ruthenium complex. The charge carrier mobilities of the polymers are strongly dependent on the metal complex content, and the results are summarized in Table 1.

The hole carrier mobilities of polymers **25a–f** and **26a–c** are similar, and are in the order of 10^{-5} to $10^{-4}\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$. Compared to other organic polymers, these series of polymers exhibit higher electron carrier mobilities, which was attributed to the presence of oxadiazole and ruthenium complex moieties. For the polymers with the same metal content, those polymers with the oxadiazole moieties at the 5,5′-positions exhibited higher charge carrier mobilities. By comparing polymers **25a–f**, it can also be seen that both hole and electron carrier mobilities increase by one order of magnitude when the ruthenium content was increased from 10 to 100% per repeating unit. These polymers were fabricated into light emitting devices. The EL and PL spectra of polymers **25d** and **25f** are shown in Fig. 14. From these spectra, it can be seen that the polymers consist of two light emitting groups: the conjugated main chain and the ruthenium complex. When the ruthenium content is low (polymer **25a**), the emission band is dominated by the π*–π emission centered at 590 nm, and the emission from the ruthenium complex MLCT state appeared as a small shoulder that extends beyond 650 nm. On the other hand, for polymer **25f** with higher metal content, the EL spectrum is dominated by an emission band centered at 690 nm. No emission from the conjugated main chain was observed. Similar to polymer **23a–e**, it was attributed to the quenching of the main chain emission by the low-lying MLCT states.

Table 1
Electron and hole carrier mobilities of different ruthenium containing conjugated polymers with 1,3,4-oxadiazole moieties on the main chain [54]

Polymer	*x*	*y*	Hole carrier mobility, μ_h ($\times 10^{-4}\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$)	Electron carrier mobility, μ_e ($\times 10^{-4}\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$)
25a	0.1	0.9	0.47	0.50
25b	0.25	0.75	0.55	0.57
25c	0.35	0.65	1.8	3.1
25d	0.5	0.5	1.5	3.6
25e	0.65	0.35	4.9	7.9
25f	1	0	5.1	8.3
26a	0.25	0.75	0.21	0.33
26b	0.5	0.5	0.45	1.5
26c	1	0	0.64	3.2

2.4. Conjugated polymers with benzoxazole, benzothiazole, and benzimidazole moieties on the main chain

Some aromatic conjugated polymers with heterocyclic systems exhibited excellent thermal stabilities due to the presence of highly rigid polymer main chain. Typical examples are poly(benzobisoxazole) (PBO), poly(benzobisthiazole) (PBT) and their derivatives. PBO and PBT are known to exhibit excellent solvent resistance, oxidative stabilities, and mechanical strength. Some of them even exhibited decomposition temperatures beyond 600 °C, which is higher than some commonly used aromatic polyamides [55,56]. In addition, the optical, luminescence, and electrical properties of other PBO type polymers were also reported [57–61]. The first example of PBO and PBT incorporated with 2,2′-bipyridine moieties was reported in 1998 [62]. The polymers (**32a**–**c** and **33a**–**c**) were synthesized by the reaction between 2,2′-bipyridine-4,4′-dicarboxylic acid 27 or 2,2′-bipyridine-5,5′-dicarboxylic acid 28 with diaminobenzenediols (**29** and **30**) or diaminobenzenedithiol **31** in the presence of polyphosphoric acid, which served as a solvent, catalyst, and dehydrating agent in the reaction (Fig. 15). The metal free polymers are only soluble in acidic solvents such as methanesulfonic acid, cone, sulfuric acid, trifluoroacetic acid, formic acid, and nitromethane/$AlCl_3$. Thermal gravimetric analysis results showed that they have excellent stabilities that are comparable to other PBO derivatives reported in the literature. The thermal gravimetric analysis thermograms of some polymers are shown in Fig. 16, and the data are summarized in Table 2. The results obtained are consistent to those published in another paper, which reported the synthesis of a series of PBO derivatives

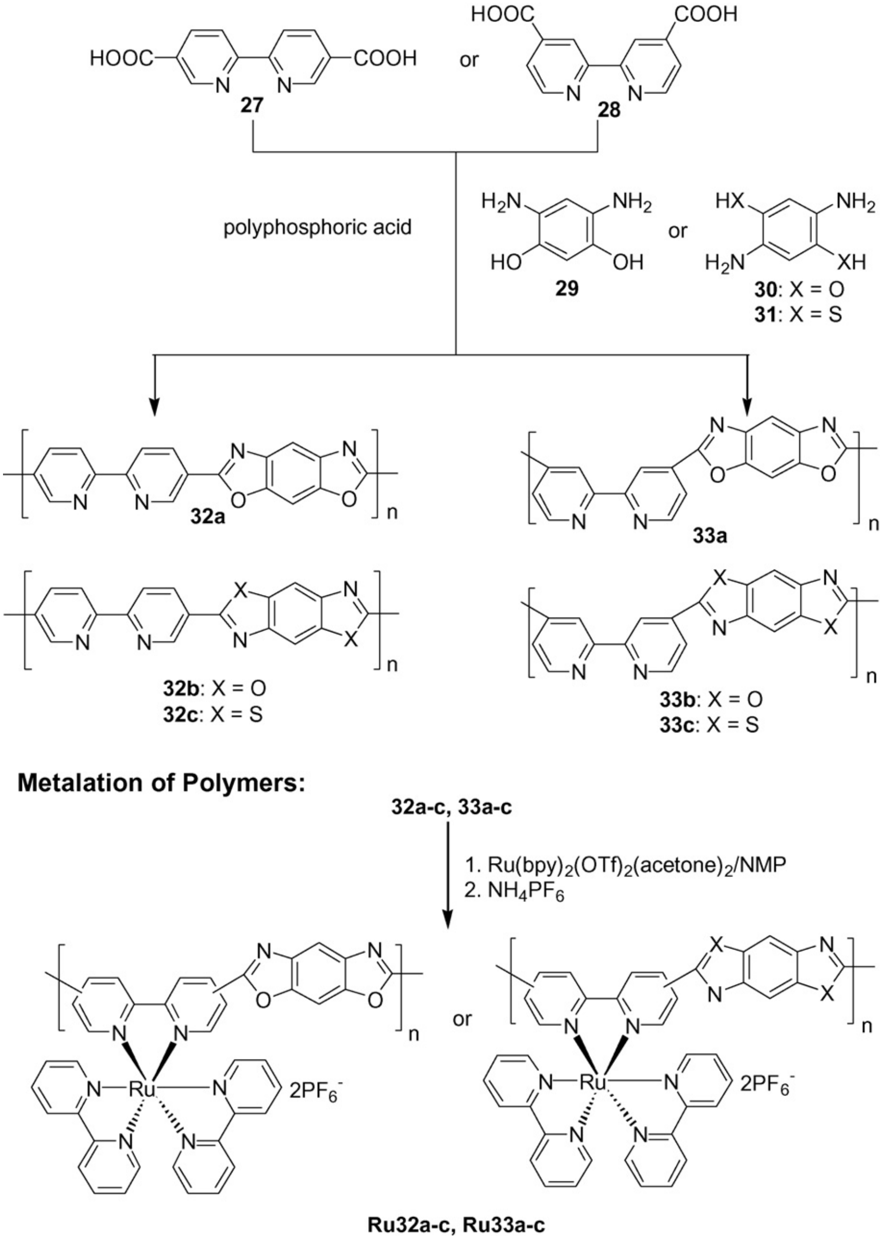


Fig. 15. Synthesis of various bipyridine containing PBO and PBT derivatives.

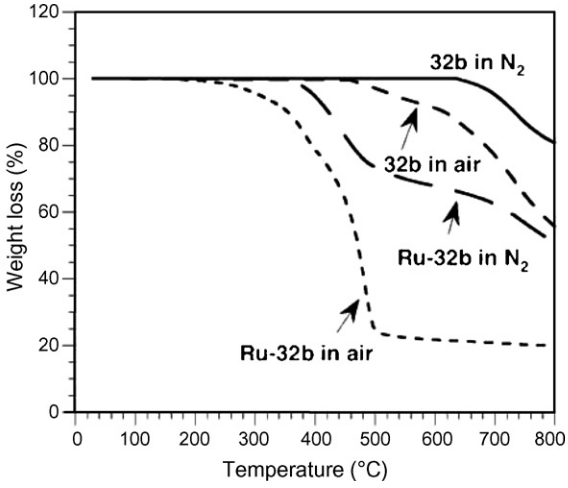


Fig. 16. TGA thermograms of bipyridine containing PBO **32** and its ruthenium complex in air and in nitrogen atmosphere. The figure was reproduced from Ref. [62], with permission from the American Chemical Society.

Table 2
Properties of polymers **32a–c** and **33a–c** [62]

Polymer	Decomp. temp, in air (°C)[a]	Decomp. temp, in N_2 (°C)[a]	Inherent viscosity (dL/g)[b]	$\lambda_{max,abs}$ (nm)
32a	657	691	5.2	408, 430
32b	591	668	3.1	406
32c	537	585	3.7	398
33a	608	668	2.1	348
33b	586	648	1.7	372
33c	569	597	2.1	378

[a] Measured by thermal gravimetric analyzer.
[b] Measured in methanesulfonic acid at 30 °C with conc. = 0.25 g/dL.

with very similar structures [63]. Due to the presence of highly rigid polymer main chain, polymers **32a–c** exhibited lyotropic liquid crystal properties in methanesulfonic acid solutions. The critical concentration for the formation of mesophases is approximately 3–4 wt.%. Polymer **32c** exhibited the highest clearing temperature (140 °C for a 10 wt.% solution) among the three polymers.

All the polymers can form ruthenium bipyridine complexes by treating the polymer with $Ru(bpy)_2(OTf)_2(acetone)_2$ in NMP. The ruthenium complex contents of **Ru32a–c** (46–69% per repeating unit) were higher than those of **Ru33a–c** (21–30%). All the metalated polymers were soluble in polar solvents such as DMF, NMP, and DMSO due to the presence of ionic moieties on the main chain. Polymer ruthenium complex **Ru32b** and **Ru32c** showed the best film forming properties, and their charge carrier mobilities were measured. Both the electron and hole carrier mobilities are in the order of 10^{-5} cm^2 V^{-1} s^{-1}, and the electron carrier mobilities are slightly higher than the hole carrier. The ruthenium complexes may be involved in the charge transport process.

Like the PBO and PBT, conjugated polymers with benzimidazole moieties can also be synthesized by the reaction between aromatic tetraamine and dicarboxylic acid monomers. Conjugated polymer **34** with bidentate benzimidazole moieties was synthesized and the resulting polymer was coordinated with the $Ru(bpy)_2^{2+}$ moieties (Fig. 17) [64]. The redox properties of polymer **35** were studied by cyclic voltammetry. It was found that the polybenzimidazole main chain was involved in electron transfer between Ruthenium sites. The electron transport process was facilitated by the electronic interaction between metal centers through the polymer main chain, rather than hopping via the main chain.

The synthesis of a polybenzimidazole with a tridentate ligand on the main chain has been reported [65]. Polymer **36** was synthesized by the reaction between pyridine-2,6-dicarboxylic acid and 3,3′-diaminobenzidine tetrahydrochloride in the presence of polyphosphoric acid (Fig. 18). The resulting polymer was soluble in organic acidic and NMP, and could form optical quality films by spin coating or solution casting. Metal complexation was carried out by treating the polymer with complexes **37a** or **37b**, yielding **Ru36a** and **Ru36b**, respectively. These polymer metal complexes have higher solubility in DMF compared to polymer **36**, owing to the presence of ionic ruthenium complex moieties on the main chain. From elemental analysis, the ruthenium complex content was estimated to be higher than 90% per repeating unit. The luminescence properties of the metal free polymer **36** were affected by the formation of aggregates. By blending the polymer with different amount of poly(vinyl alcohol), different emission spectra were observed. Polymer **36** was fabricated into single-layered light emitting devices, which exhibited light emission due to the π*–π emission from the main chain. An external quantum efficiency of 0.1% was measured.

3. Metal containing non-conjugated polymers with rigid main chain

3.1. Aromatic polyamides and polyesters

A series of aromatic polyamides **38a–g** with 2,2′-bipyridyl moieties was synthesized by the reaction between aromatic

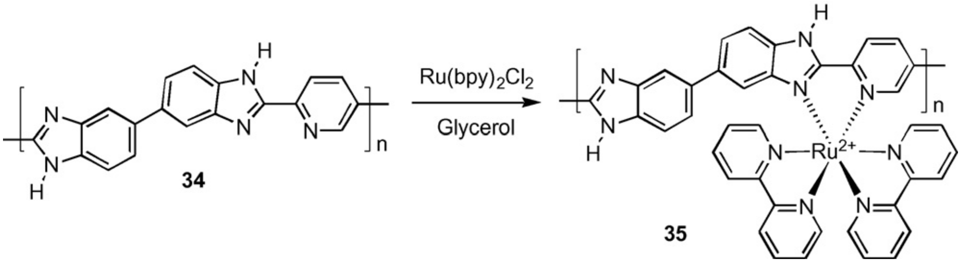


Fig. 17. Synthesis of ruthenium containing conjugated polymer **35** with bidentate benzimidazole moieties.

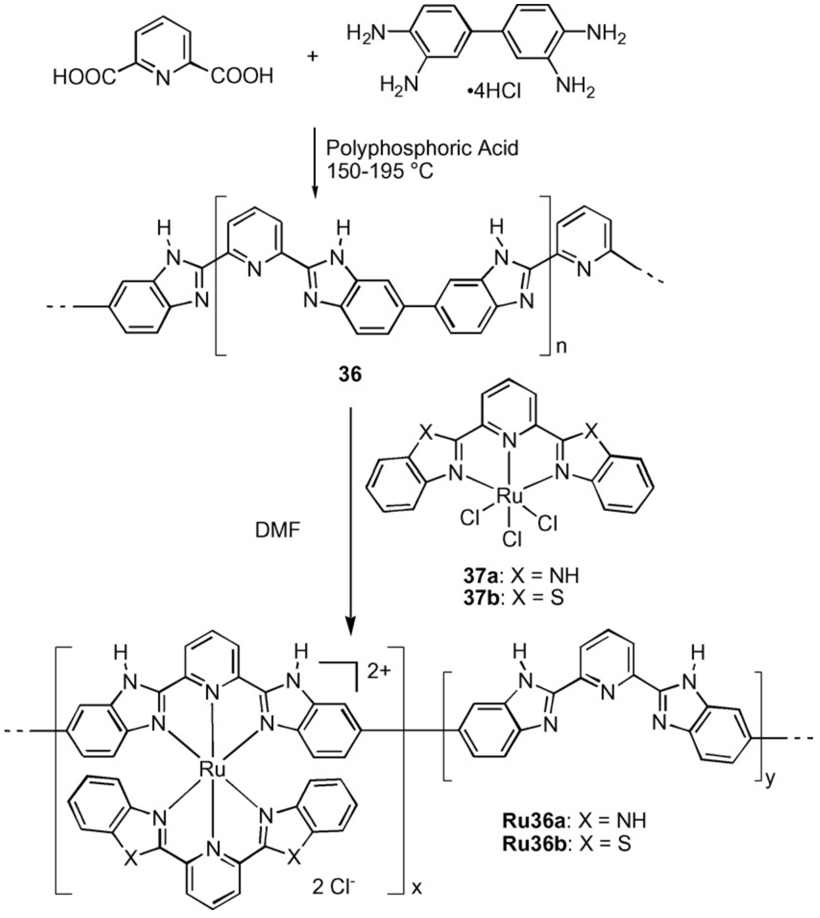


Fig. 18. Synthesis of ruthenium conjugated polymers **Ru36a**–**b** with tridentate benzimidazole moieties.

diamines and 2,2′-bipyridine-5,5′-dicarboxylic acid in the presence of triphenylphosphite and pyridine as the condensing agents (Fig. 19) [66]. These polymers contain a highly rigid main chain, and the polymerization could only be carried out in hexamethylphosphoramide (HMPA)–LiCl mixture as the solvent. The polymers exhibited modest to excellent thermal stabilities, and their decomposition temperatures (in the range of 380–498 °C) are dependent on the rigidity of the main chain. When dissolved in HMPA–4% LiCl or cone. H_2SO_4 solution, some polymers exhibited lyotropic liquid crystal phases. For polymer **38b** that has the most rigid main chain, the critical concentration for the formation of lyotropic mesophases was as low as 1 wt.%, which was significantly lower than those of some extensively studied aromatic polyamides [67]. In a later report [68], more examples of aromatic polyamides were synthesized by the similar method, and the thermotropic and lyotropic liquid crystal properties of the polymers were studied in detail. For some polyamides with a short segment of flexible linkage on the main chain, they exhibited both thermotropic and lyotropic mesophases. In the same paper, the synthesis of different aromatic polyesters **41a**–**n** and aliphatic polyesters **42a**–**n** with 2,2′-bipyridyl moieties was also reported. The polyesters were synthesized by the alcoholysis of acid chloride **39** or *trans* esterification of the diethyl ester **40**. More than 30 different aromatic and aliphatic diols were used as the comonomers (Fig. 20).

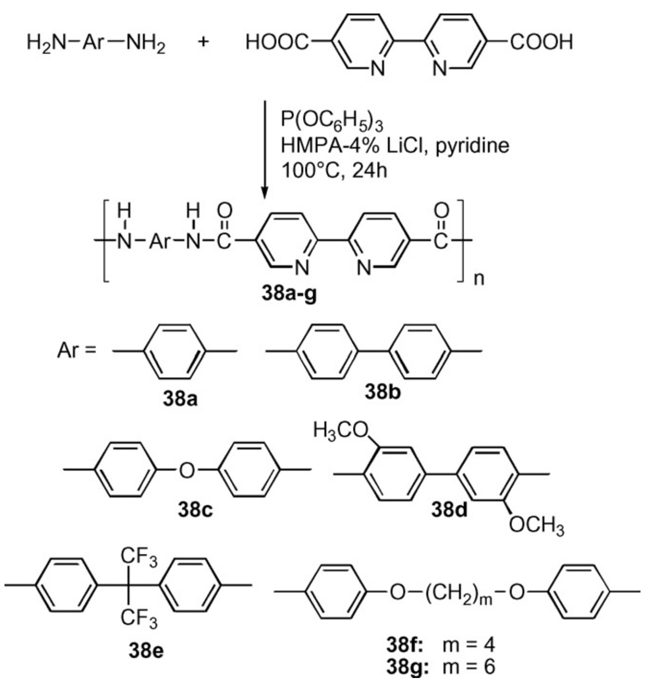


Fig. 19. Synthesis of bipyridine containing aromatic polyamides.

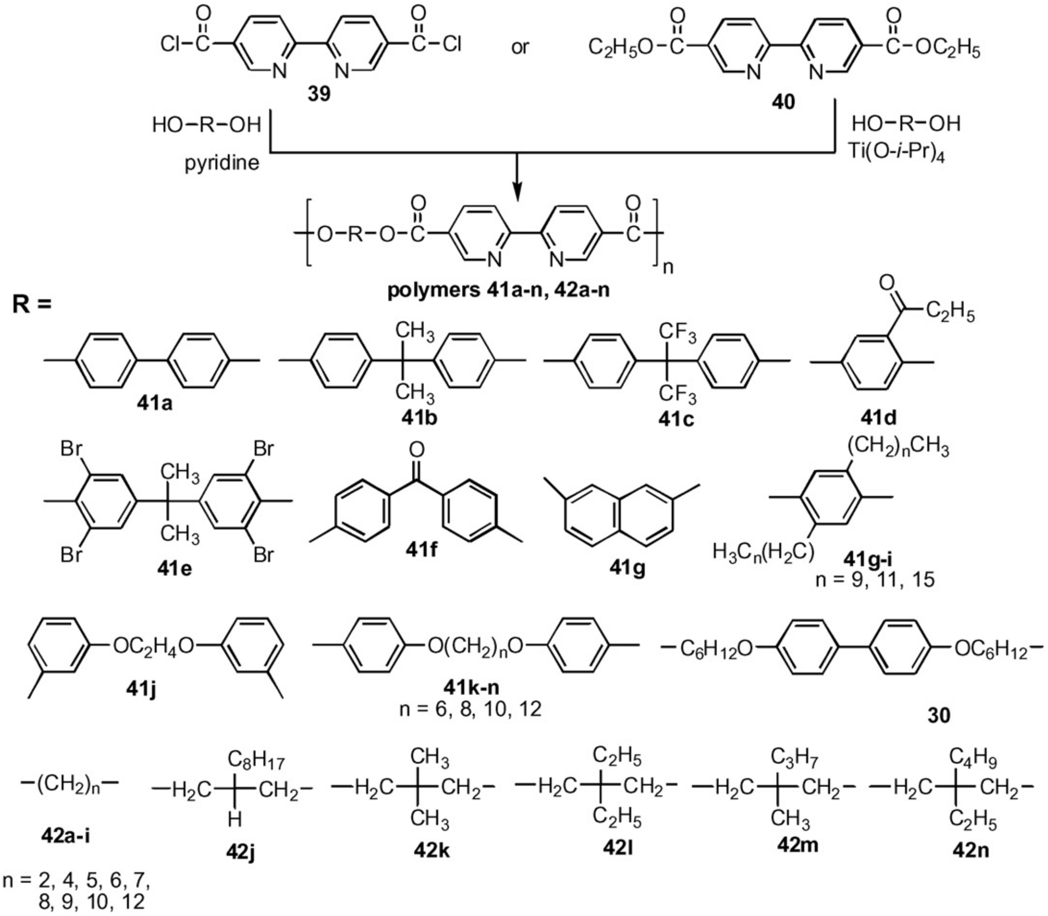


Fig. 20. Synthesis of aromatic and aliphatic polyesters with bipyridine moieties on the main chain.

Unlike the polyamide analogues, the polyesters did not exhibit lyotropic liquid crystal properties, but some polyesters with flexible main chain or side chain still exhibited thermotropic mesophases.

All these bipyridine containing polymers can form complexes with ruthenium by direct metal complexation with $Ru(bpy)_2(OTf)_2(acetone)_2$. Alternatively, the polymer-ruthenium complex can also be synthesized by the copolymerization of $Ru(dcbpy)(bpy)_2Cl_2$ (dcbpy = 2,2′-bipyridine-5,5′-dicarboxylic acid) with different diamines. Some polymer–ruthenium complexes were able to form optical quality films by solution casting method, and single layered light emitting devices (ITO/polymer/Al) were fabricated. Red light emission was observed when the devices were subjected to forward bias.

3.2. Polyimides

Polyimide is another type of important polymer with rigid main chain and good thermal stability. Polyimides have been widely used in many different technological areas such as microelectronics, coating, composites, separation membranes, and fiber applications [69]. Most of the polyimides reported to date are based on pure organic systems. Relatively little research effort was paid on metal containing polyimides. In most of the examples reported in the literature, studies in metal containing polyimides were focused on the polyimide–metal interaction and the adhesive properties of polymers on the metal surface [70–72] due to the importance of polyimides as interlayer dielectric materials in microelectronic industry. Another application of metal containing polyimides is the preparation of reflective surface, which involve the doping of metallic precursors into polyimides. The resulting polyimide films formed may be used as reflector films for radio frequency antennas, surface conducting tapes, contacts in microelectronics, etc. [73]. Polyimides that were loaded with gold or silver dopants have been reported. Silver hexafluoroacetylacetone [74], auric acid, or triethylphosphinegold(I) succinimide [75] have been used as the precursor for silver and gold. There have been few examples of synthesizing metal containing polyimides by the direct polymerization between metal complex monomers. Chan et al. reported the synthesis of different polyimides **44a–f** by using the diamino ruthenium terpyridine complex 43 and various dianhydride monomers [76]. After the synthesis of the poly(amic acid) precursors, the polyimides were obtained by the in situ ring closure imidization reaction by the addition of pyridine/acetic anhydride (Fig. 21). Despite having highly rigid main chain, the polyimides were soluble in polar solvents such as DMF, NMP, and DMSO after the imidization, which is due to the presence of ionic metal complex moieties. All the polyimides exhibited reasonably good thermal stabilities and the decomposition

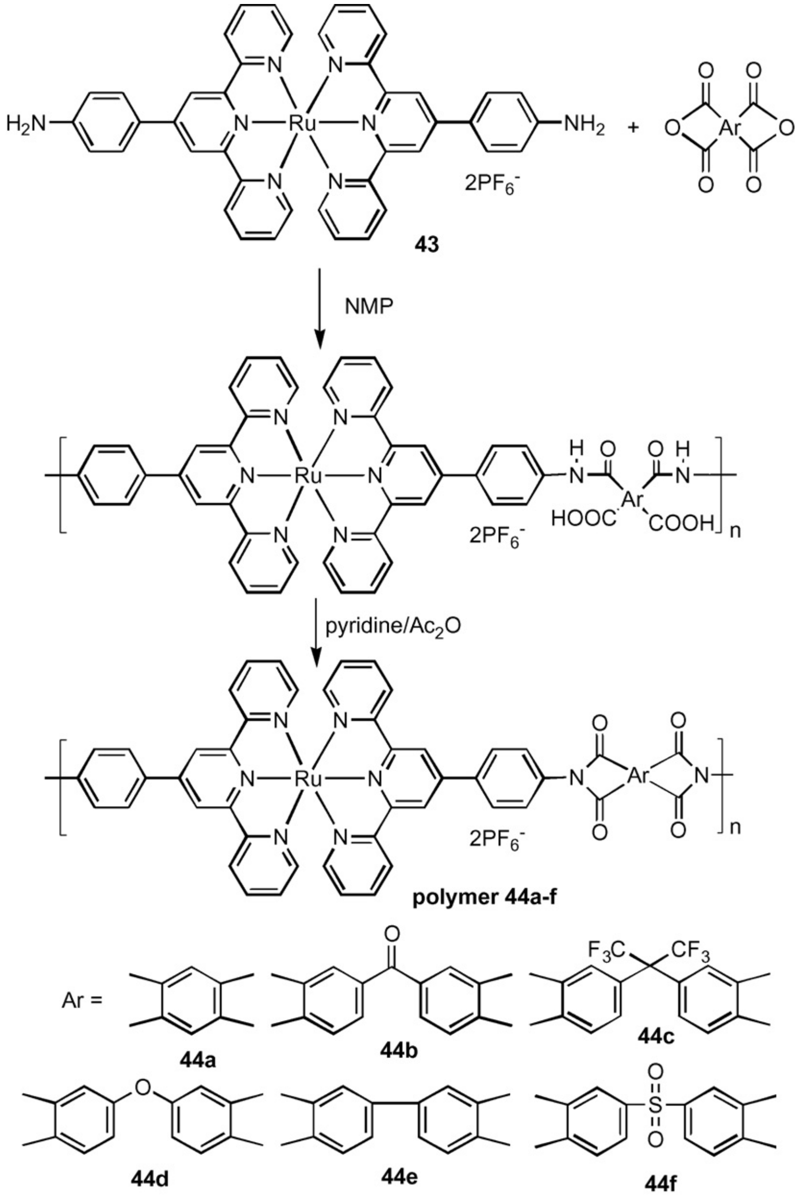


Fig. 21. Synthesis of ruthenium containing polyimides.

temperatures are in the range between 350 and 360 °C (measured under N_2). Those polymers with more rigid diimide unit (**44a** and **44e**) also exhibited higher glass transition temperature ($T_g = 231$, 228 °C) than those with flexible linkage (**44b**, **44c**; $T_g = 218$, 214 °C). The ruthenium terpyridine complex incorporated could enhance the absorption at around 500 nm due to the MLCT transition, resulting in an enhancement in photoconductivity of the polymers in the visible region. In addition to serving as photosensitizers, the ruthenium complexes may also play the role as charge transport units by facilitating the charge transport process. Some polyimides also showed emission in the near IR region, which was assigned to be the emission from the charge transfer states. In a later report, a series of chlorotricarbonylrhenium(I) diimine complex containing polyimides was synthesized by the same approach [77]. The polymers also showed enhanced photoconductivity in the visible region by the rhenium complexes on the polymer main chain.

4. Conclusions

The syntheses of different metal containing polymers with rigid main chain are presented. Different heterocyclic units such as quinoxaline, phenazine, oxadiazole, benzoxazole, benzothiazole, and benzimidazole can be used in the construction of the conjugated main chains. For non-conjugated polymers, the rigid main chains are mainly based on aromatic polyamides, polyesters, and polyimides. All these polymers are functionalized with bidentate or tridentate ligands, which can form complexes with different metals. Binding of metal ions by these ligands also forms the basis for metal ion sensing. Most of these polymers exhibit high thermal stability due to the presence of rigid main chain. The optical and electronic properties of these polymers can be fine tuned by adjusting the metal content. These metal containing polymers have found potentials in optoelectronic applications such as light emitting diodes, nonlinear optics, photodetectors, and solar cells. It is envisaged that the polymers are able to serve many other functions when a suitable metal complex moiety is incorporated. This functional design approach provides an effective methodology in developing new materials for advanced technology.

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