

Polyfluorenes with On-Chain Metal Centers

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Abstract Polyfluorenes containing metal complexes, especially phosphorescent heavy-metal complexes, are a type of important optoelectronic materials. The present review summarizes the synthesis and optoelectronic properties of polyfluorenes with phosphorescent heavy-metal complexes on the chain. Efficient energy transfer from polymer main-chain to metal centers occurs in these host–guest systems. The promise of strong emission and the easiness for processing in organic electronic devices provide incentives to develop these materials intensively. The range of applications of these materials spans the whole field of interaction between light and electricity. Especially, attention is given to the interesting optoelectronic properties and promising applications in organic light-emitting diodes (OLEDs), memory devices, and sensors.

Keywords Energy transfer · Metal complexes · Optoelectronic devices · Polyfluorenes

Abbreviations

Alq3	Al(III) triquinolinolate
bpy	2,2'-Bipyridine
BT	Benzothiadiazole
Cz	Carbazole
EL	Electroluminescence
LEC	Light-emitting electrochemical cell

MLCT	Metal-to-ligand charge-transfer
OLED	Organic light-emitting diode
PBD	2-(4-Biphenyl)-5-(<i>t</i> -butylphenyl)-1,3,4-oxadiazole
PEDOT	Poly(3,4-ethylenedioxythiophene)
PF	Polyfluorene
PL	Photoluminescence
PLED	Polymer light-emitting diode
PPV	Poly(phenylvinylene)
PT	Polythiophene
PtTPP	Pt(II) tetraphenylporphyrin
PVK	Polyvinyl carbazole
WORM	Write-once read-many-times
WPLED	White polymer light-emitting diode

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Introduction

In recent years, conjugated polymers containing metal complexes, especially phosphorescent heavy-metal complexes, have attracted increasing attention, since the utility of phosphorescent heavy-metal complexes can increase the luminescence efficiency in optoelectronic applications by harvesting the large percentage of triplet excitons created upon electron–hole recombination [1–5]. The energy can be transferred efficiently from conjugated main-chain (as host materials) to metal complexes (as guest) in the main- or side-chain of polymers. In addition, polymers with on-chain metal centers can efficiently avoid the intrinsic defects in corresponding blend system, such as phase-separation [6].

Current widely studied conjugated polymers include poly(phenylvinylene) (PPV), polythiophene (PT), and polyfluorene (PF). Although PPV and its derivatives have high photoluminescence (PL) and electroluminescence (EL) efficiencies, they usually suffer from photooxidative degradation [7]. Compared with PPV, PT and its derivatives have low PL and EL efficiencies [8]. So far, polyfluorenes have emerged as the most attractive blue-emitting materials due to their high efficiency, charge transport properties, and good chemical and thermal stability [9–15]. Therefore, they are usually selected as host materials for phosphorescent heavy-metal complexes [16–18]. The most important criterion for serving as phosphorescent host is that triplet energy level of host materials should be above that of dopant in order to satisfy exothermic energy transfer. This is a crucial factor for achieving high phosphorescence efficiency in the host–guest system [19]. The triplet energy level of polyfluorene derivatives is about 2.15 eV [20], which renders them act as the efficient host for red-light emitting phosphors, but the photoluminescence efficiencies will be reduced when used as the host for green-light and yellow-light emitting phosphors. Nevertheless, the triplet energy level of polyfluorenes can be tuned through modifying their chemical structure.

To date, there have been numerous examples of polyfluorenes incorporating phosphorescent heavy-metal complexes, including iridium(III) (Ir), platinum(II) (Pt), europium(III) (Eu), rhenium(I) (Re), and ruthenium(II) (Ru) complexes. The polymers are usually prepared by Suzuki-type or Yamamoto-type polymerization method of fluorene monomers and complex monomers containing active groups on ligands. In this review, we will concentrate on their preparation, optical properties, as well as applications in optoelectronic devices. Meanwhile, the feature of intramolecular interaction between polymer and metal complex is elucidated; the advantages of these polymeric phosphorescent materials serving as organic light-emitting diodes (OLEDs) component are illustrated.

2

Polyfluorenes Containing Iridium(III) Complexes

Among phosphorescent metal complexes, Ir(III) complexes have been considered as one of the best phosphorescent material candidates because they show intense phosphorescence at room temperature and significantly shorter emission lifetime compared with other heavy-metal complexes, which are crucial for utility of phosphorescent materials. Moreover, the emission colour can be tuned easily over the entire visible region by simply modifying the chemical structures of ligands [21–23].

Ir(III) complexes can be divided into two classes. One class includes the neutral complexes containing cyclometalated ligands and other anionic ligands. The other class includes charged Ir(III) complexes containing neutral bidentate ligands (e.g., bipyridine and phenanthroline derivatives). Correspondingly, the subsequent discussion of polyfluorenes containing Ir(III) complexes can be also divided into two parts, namely, polyfluorenes with neutral Ir(III) complexes and with charged complexes in the chain. Furthermore, a major subdivision arises from a consideration of the location of the Ir(III) centres; these can be either in the main-chain or in the side-chain.

2.1

Polyfluorenes with Neutral Iridium(III) Complexes

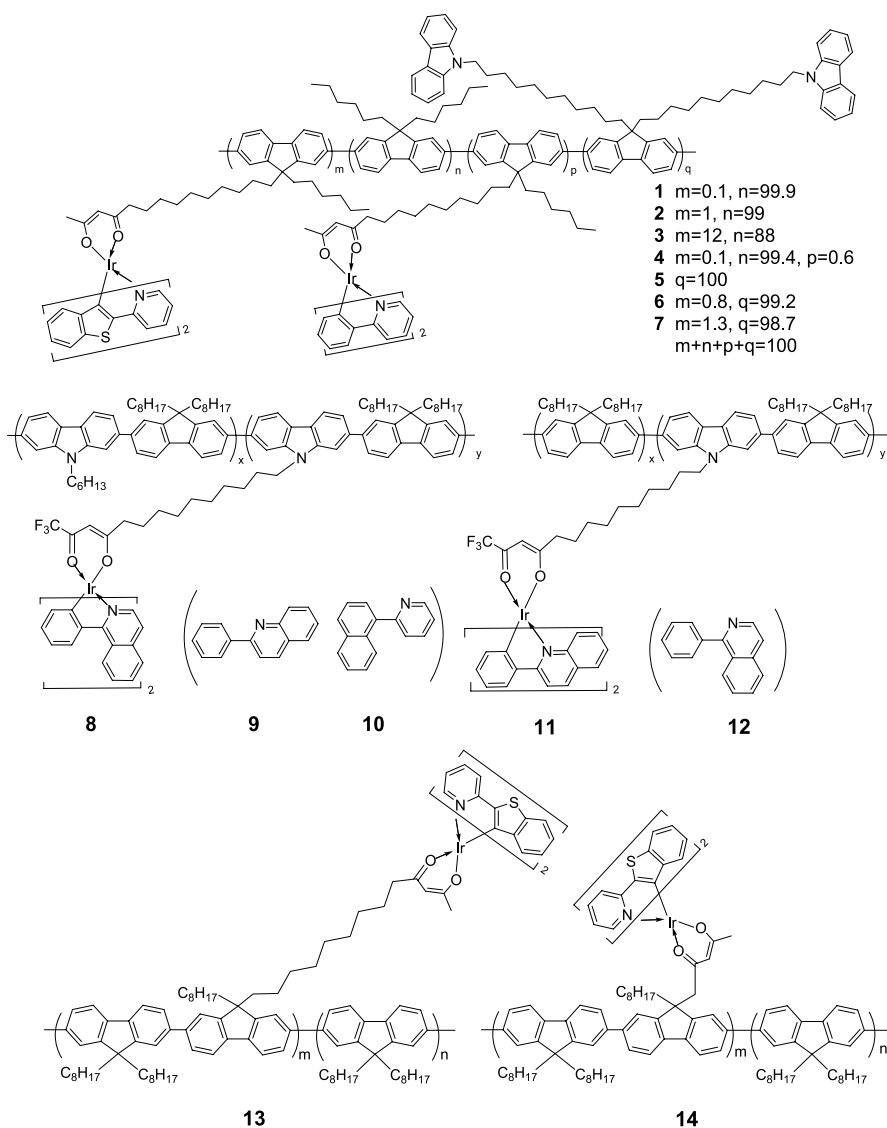
Polyfluorenes with neutral iridium(III) complexes in the side-chain and main-chain of polymers are discussed, respectively.

2.1.1

Polyfluorenes with Neutral Iridium(III) Complexes in the Side-Chain

Introducing Ir(III) complexes into the side-chain using a chemical bond is an effective way to produce polyfluorenes with on-chain iridium cen-

tres. Chen et al. [4] first reported high-efficiency red-light emission from polyfluorenes grafted with cyclometalated iridium complexes (polymer 1–7). These polymers were prepared by Suzuki-type or Yamamoto-type polymerization method. Polymer 7 based device showed red emission with highest efficiency of 2.8 cd/A at 7 V. The incorporation of carbazole (Cz) can significantly increase the efficiency and lower the turn-on voltage. They demon-



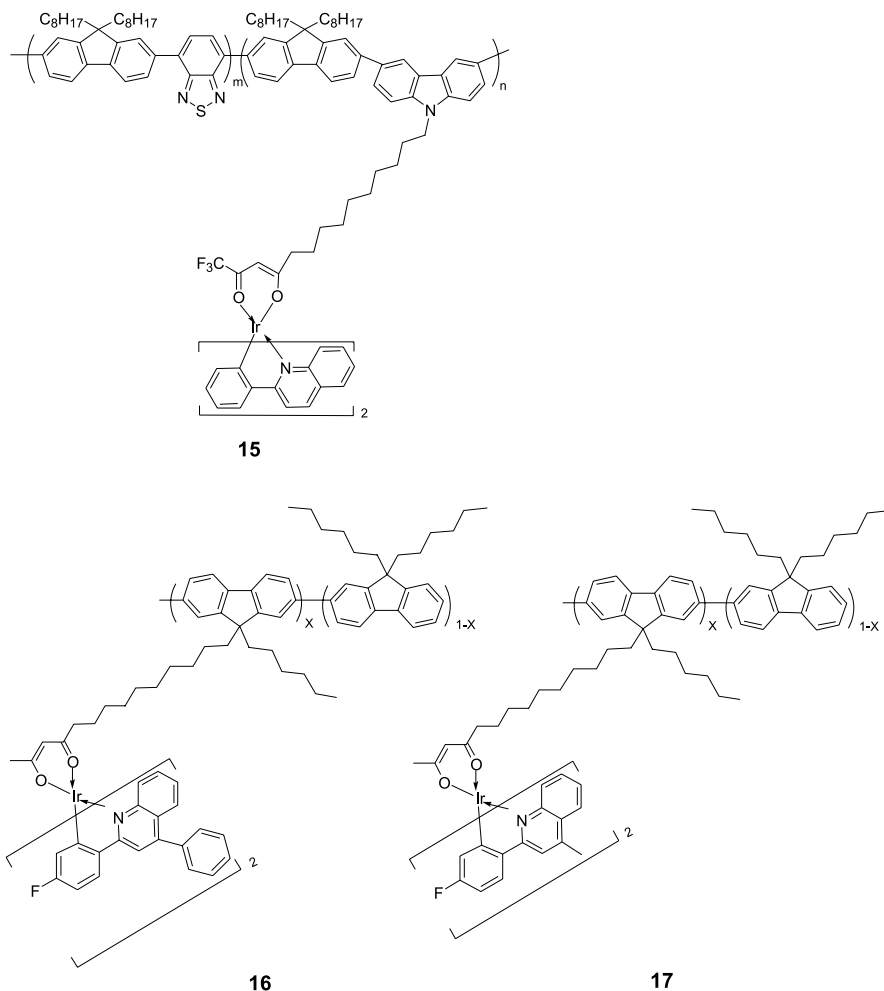
Scheme 1 Polyfluorene derivatives with Ir(III) complex on the side-chain

strated that both the energy transfer from PF main chain and from an electroplex formed between main-chain fluorene and side-chain carbazole moieties to the red Ir(III) complex can significantly enhance the device performance.

Subsequently, Yang et al. also prepared a series of fluorene-alt-carbazole copolymers grafted with cyclometalated Ir(III) complexes (polymer 8–12) [24]. The red-light emitting devices were realized and showed the highest external quantum efficiency of 4.9% ph/el, the luminous efficiency of 4.0 cd/A, and a peak emission of 610 nm.

Proper conformation between the Ir(III) complex guest and the fluorene segment host will play an important role in the energy transfer between the two parts [25]. The face-to-face conformation is beneficial to π - π interactions between host and guest [25], which are known to be the key requirement for Dexter triplet energy transfer [26]. The conformation may be determined by the length of side-chain. Thus, the incorporation of different alkyl between the polymer host and phosphorescent guest is an important design principle for achieving high efficiencies in those electrophosphorescent organic light-emitting diodes for which the triplet energy levels of the host and guest are similar [25]. The investigation of the property–structure relationship of polymer 13 and 14 confirmed that long alkyl between the polymer host and phosphorescent guest might be helpful in suppression of the back transfer of triplets from the red phosphorescent iridium complex to the polyfluorene backbone, which could result in higher photo- and electroluminescence efficiencies.

White polymer light-emitting diodes (WPLEDs) have been attracting increasing attention because they can be easily fabricated using wet processes, including the spin-coating, screen printing, and ink-jet printing techniques, which are expected to be lower in cost in mass production, especially in the production of large-area panel displays. Therefore, it is desirable to obtain white-light emission from a single-component material, so as to avoid drawbacks of polymer-blend or small-molecule-doped polymer systems. White-light emission could be obtained from a single polymer with three individual emission species by introducing a small number of Ir(III) complexes into the side chain [27]. In polymer 15, fluorene is used as the blue-emissive component, benzothiadiazole (BT) and the Ir(III) complex act as green-emissive and red-emissive chromophores, respectively. By changing the contents of BT and Ir(III) complex in the polymer, the electroluminescence spectrum from a single polymer can be adjusted to achieve white-light emission. The devices exhibit a maximum luminance efficiency of 6.1 cd/A at a current density of 2.2 mA/cm². A maximum luminance of 10 110 cd/m² was achieved at a current density of 345 mA/cm². Introducing orange phosphorescent iridium complex into polyfluorene can also obtain white-light-emitting polymers (polymer 16 and 17) [28]. Tuning the content of Ir(III) complex in the polymer 16, WPLEDs with a maximum luminous efficiency



Scheme 2 White light-emitting polymers based on polyfluorene derivatives with Ir complex on the side-chain

of 4.49 cd/A and a maximum power efficiency of 2.35 lm/W at 6.0 V were realized.

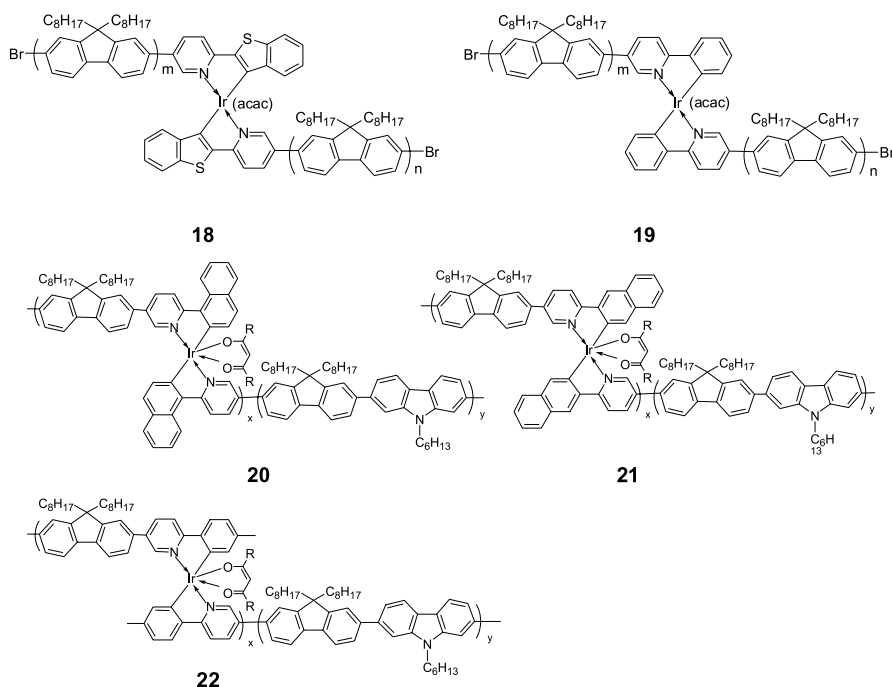
2.1.2

Polyfluorenes with Neutral Iridium(III) Complexes in the Main-Chain

Polyfluorene with Ir(III) complexes in the main-chain can be obtained by chelating iridium with C[^]N ligand introduced into the polyfluorene main-chain [5, 29, 32]. Oligo- and poly(9,9-dioctylfluorenyl-2,7-diyl) with red or green Ir(III) complexes in the main-chains were first reported by Holmes et al.

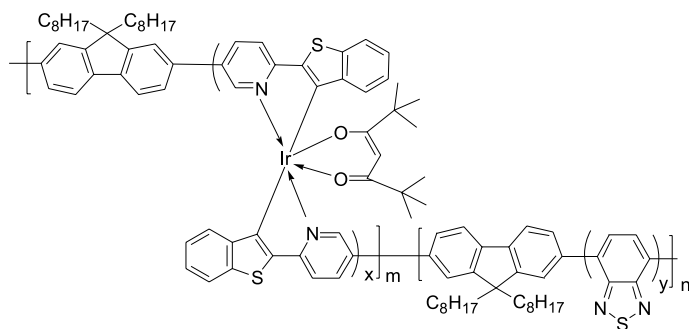
(polymer **18** and **19**) [5]. The efficiencies of the green devices are moderate, but the devices still represent improvements over blended composite materials of organometallic phosphors in polyfluorene host. The red light-emitting devices with better triplet energy level matching between iridium complex and fluorene energy levels show significant improvements in device efficiency.

Subsequently, Cao et al. [30, 31] designed and synthesized polymer **20–22** by similar method and the highly efficient saturated red-phosphorescent polymer light-emitting diodes (PLEDs) were achieved on the basis of copolymer **20**. The best device performances are observed with an external quantum efficiency of 6.5% photon/electron (ph/el) at the current density of 38 mA/cm², with the emission peak at 630 nm ($x = 0.65$, $y = 0.31$) and the luminance of 926 cd/m².



Scheme 3 Chemical structures of polyfluorenes with on-chain Ir complexes

Introducing red-light emitting Ir(III) complex and BT into the main-chain of polyfluorene (polymer **23**) can realize white-light emission. A WPLED with a structure of ITO/PEDOT:PSS/PVK/polymer **23**/CsF/Al showed a maximum external quantum efficiency of 3.7% and the maximum luminous efficiency of 3.9 cd/A at the current density of 1.6 mA/cm² with the CIE coordinates of (0.33, 0.34). The maximum luminance of 4180 cd/m² is achieved at the current density of 268 mA/cm² with the CIE coordinates of (0.31,

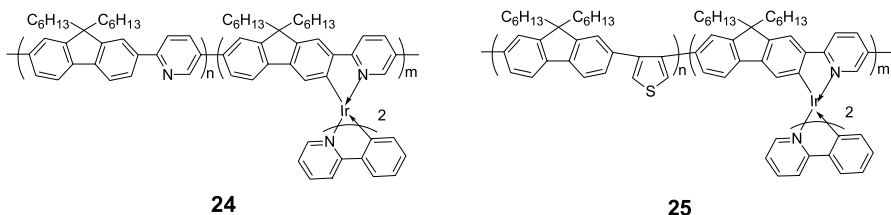


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Scheme 4 Chemical structure of white light-emitting polymer based on polyfluorene with Ir complex on the main-chain

0.32) [33]. The white-light emissions from such polymer are stable in the white-light region at all applied voltages, thus indicating that the approach of incorporating singlet and triplet species into the polymer backbone is promising for WPLEDs.

It has been proven that the triplet energy level of polyfluorene can be increased by the incorporation of other units to block the π -conjugation of polyfluorene. For example, introducing pyridine or thiophene into the polyfluorene chains can reduce the effective conjugation, increasing the energy level of the polymer (polymer 24 and 25) [29]. For 24, the triplet energy of host poly(9,9-dihexylfluorene-*alt*-2,5-pyridine) is low, resulting in quenching of the excited triplet state of the iridium complex by energy transfer to the triplet of the polymer backbone. This would result in quenching of emission from the phosphor and low quantum efficiencies. However, exchanging the 2,5-linked pyridine group with the 3,4-linked thiophene group resulted in the increase of triplet energy of host (polymer 25). Thus, the possibility of triplet energy transfer from an excited-state phosphor to the non-emitting triplet state of the backbone is reduced and quantum efficiencies increase significantly.

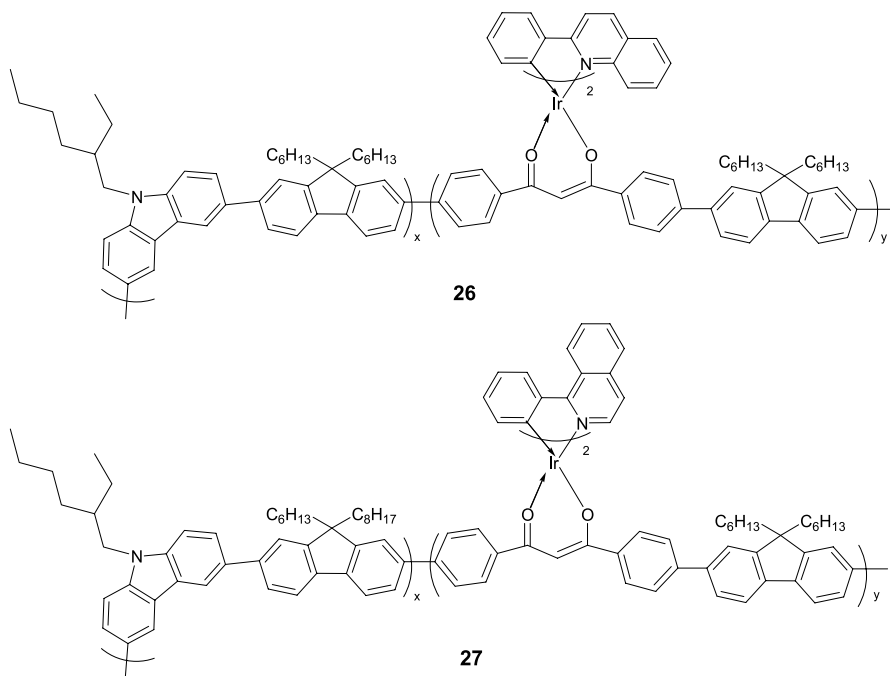


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Scheme 5 Chemical structures of polyfluorenes with on-chain Ir complexes containing pyridine or thiophene on the main-chain

Another way to introduce Ir(III) complexes into the main-chain of polyfluorenes was realized by Suzuki polycondensation of fluorene segments and β -diketone ligand chelated with Ir(III) chloride-bridged dimer (polymer 26 and 27) [34, 35]. A saturated red-emitting polymer light-emitting diode was achieved from the device ITO/PEDOT/polymer 27 + PBD (40%)/Ba/Al with the maximum external quantum efficiency of 0.6% at the current density (J) of 38.5 mA/cm² and the maximum luminance of 541 cd/m² at 15.8 V.



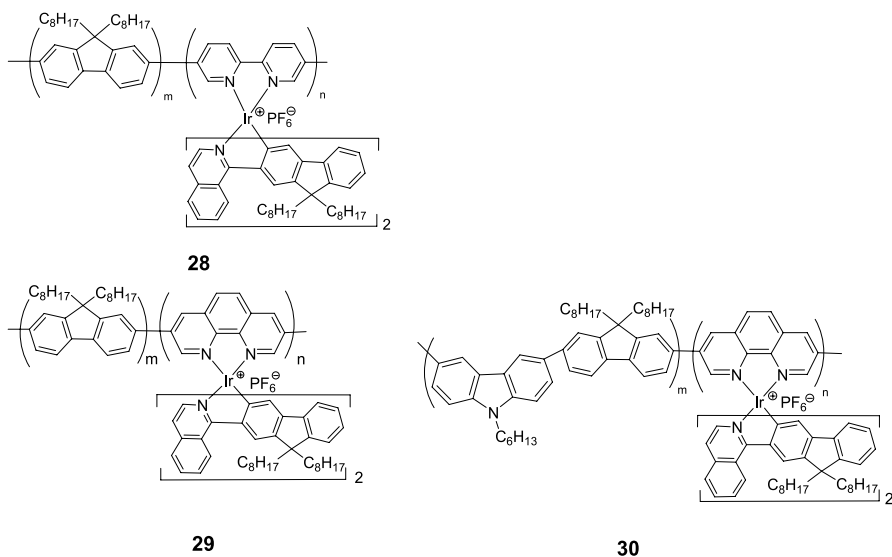
Scheme 6 Chemical structures of polyfluorenes with Ir complexes on the main-chain

2.2

Polyfluorenes with Charged Iridium(III) Complexes

Recently, charged Ir(III) complexes have been attracting increasing attention because they provide emission centres and ionic conductivity in the same species and have some features which may make them one of the best candidates for lighting, display, and light-emitting electrochemical cells (LEC) applications [36–43].

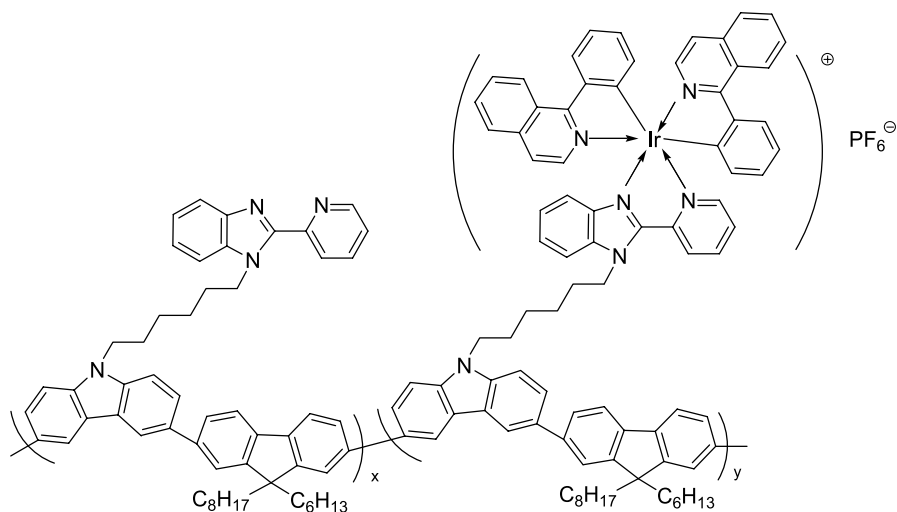
Our group [44, 45] first synthesized a series of polyfluorene derivatives (polymer 28–30) with charged red-light emitting Ir(III) complexes in the backbones, in which the phosphorescent chromophores were molecularly dispersed within the composite material. Saturated red-light emission can be



Scheme 7 Chemical structures of polyfluorenes with charged Ir(III) complexes in the main-chain

realized by choosing appropriate ligands. Cz units were also introduced into the backbones of polymer. Here, Cz would play multi-roles: as hole transport moiety on the polymer/ITO interface, as charge trapping site, and as a barrier for back energy transfer from the triplet state of Ir(III) complexes to that of host [4, 46–48]. Almost complete energy transfer from the host fluorene segments to the guest Ir(III) complexes was achieved in solid state even at the low feed ratio of complexes. Intra- and inter-chain energy transfer mechanisms coexisted in the energy migration process of this host–guest system, and the intramolecular energy transfer might be a more efficient process. Chelating polymers showed more efficient energy transfer than the corresponding blended system and exhibited good thermal stability, redox reversibility, and film formation as well. Preliminary results concerning polymer light-emitting devices indicate that these materials offer promising opportunities in optoelectronic applications.

Polyfluorene with charged Ir(III) complexes in the side-chain can be obtained by introducing N⁺N ligand into side-chain of polymer and then chelating with Ir(III) chloride-bridged dimer. Yang and Peng et al. [49] synthesized a series of copolymers with charged Ir(III) complexes in the side-chain using fluorene and Cz as segments of backbone (polymer 31). Excellent device performances were obtained using this kind of polymer as emission materials. A maximum external quantum efficiency of 7.3% and a luminous efficiency of 6.9 cd/A were achieved at a current density of 1.9 mA/cm².



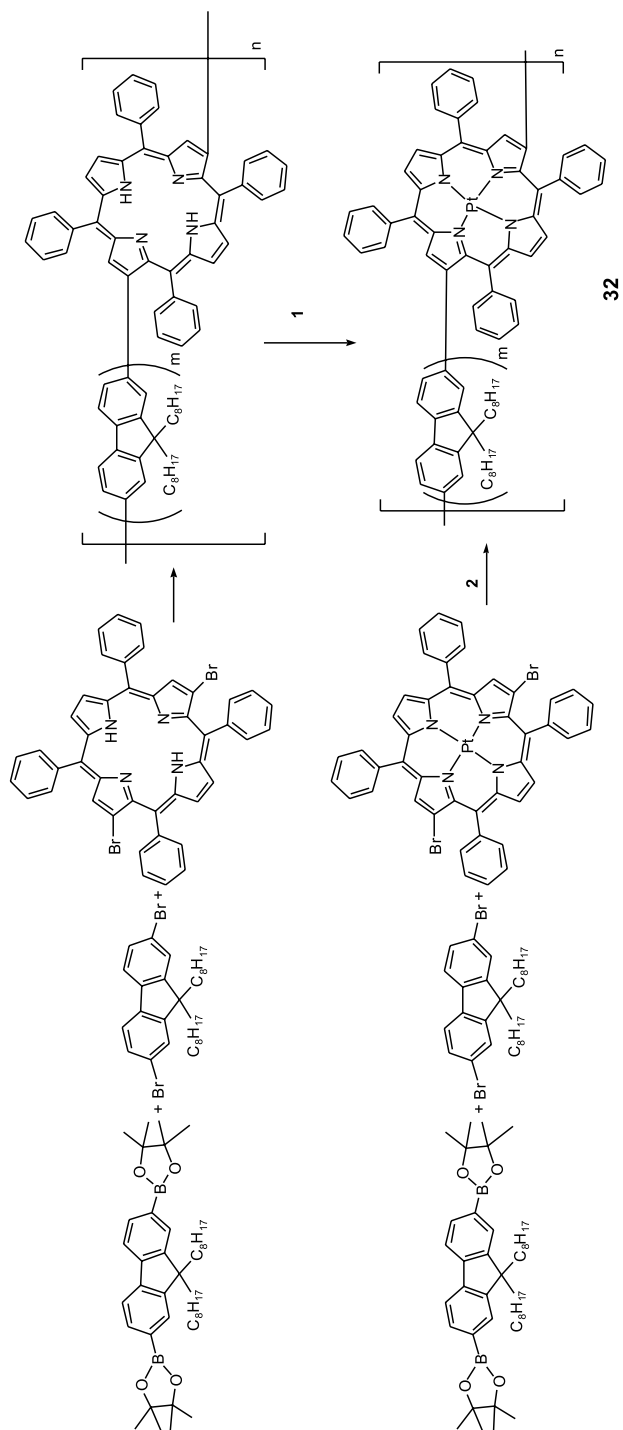
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Scheme 8 Chemical structure of polyfluorene derivatives with charged Ir(III) complex in the side-chain

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Polyfluorenes Containing Platinum(II) Complexes

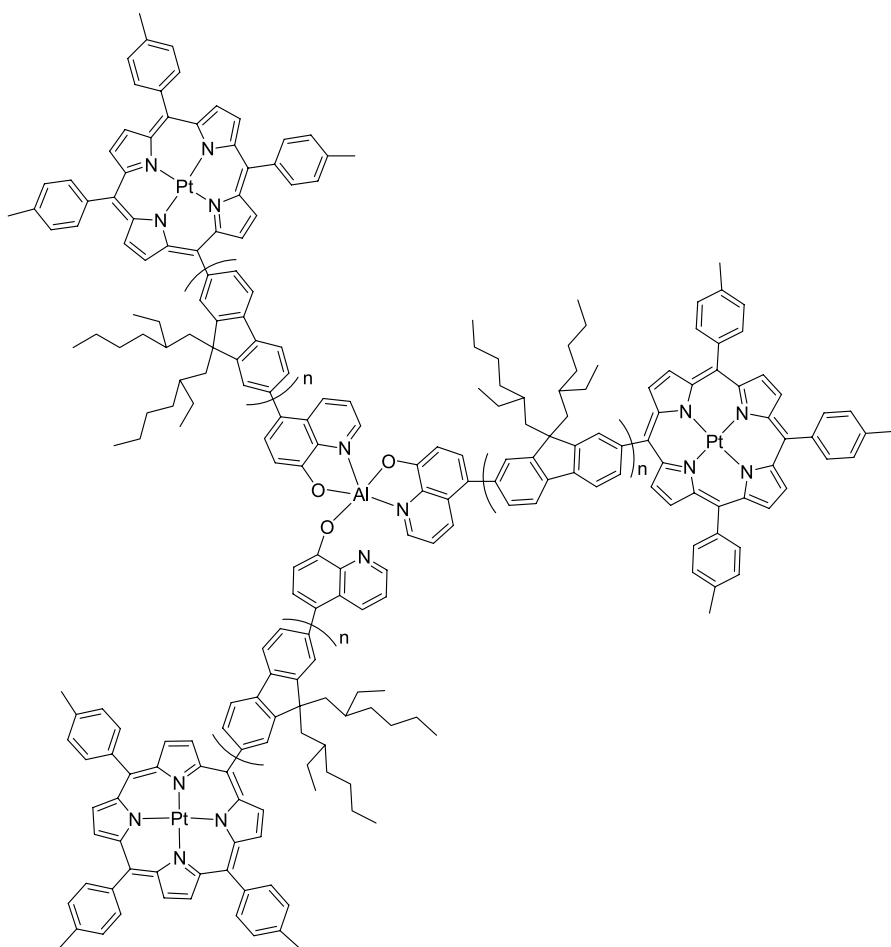
Pt(II) complexes have been studied intensively, because they show high luminescent quantum efficiency and its planar structure favors Pt–Pt interactions, which usually leads to the self-assembly behavior [50, 51]. Cao et al. [52] first reported the synthesis and photo- and electroluminescent properties of copolymers (polymer 32) containing tetraphenylporphyrin Pt(II) (PtTPP) complexes in the polymer main-chain derived from direct metalation reaction of the copolymers from metal-free poly(fluorene-*co*-tetraphenylporphyrin) (route 1 in Scheme 9). Moreover, it provides flexibility to shift from one metal ion to another with a single type of metal-free porphyrin copolymer [53]. The copolymers gave deep red emission. The highest external quantum efficiency of the devices based on the Pt(II) complex (1 mol % PtTPP in copolymer) was 0.43% with emission peaking at 676 nm. This kind of polymer can also be obtained through the copolymerization of monomeric porphyrin–platinum(II) complexes and dialkylsubstituted fluorene monomers by Suzuki coupling reaction (route 2 in Scheme 9). The device based on the porphyrin–platinum(II) copolymer (with 5 mol % PtTPP in the copolymer) showed the highest external quantum efficiency of 1.95% in an ITO/poly(3,4-ethylenedioxythiophene)/PVK/70 : 30 (w/w) polymer:PBD/Ba/Al device configuration. In comparison with the copolymers



- ◀ **Scheme 9** Synthesis routes of polyfluorenes with on-chain Pt(II) complexes by post-polymerization metalation (route 1) and copolymerization from Pt(II) metal complexes (route 2)

synthesized via a postpolymerization metalation route, copolymerization from Pt(II) complexes proved to be a more efficient synthetic route for high-efficiency electrophosphorescent polymers [54].

Recently, Anzenbacher et al. [55, 56] first demonstrated molecular wire behavior occurring in solid state and in functional OLEDs in donor-bridge-acceptor triads consisting of Al(III) triquinolinolate (Alq_3), oligofluorene

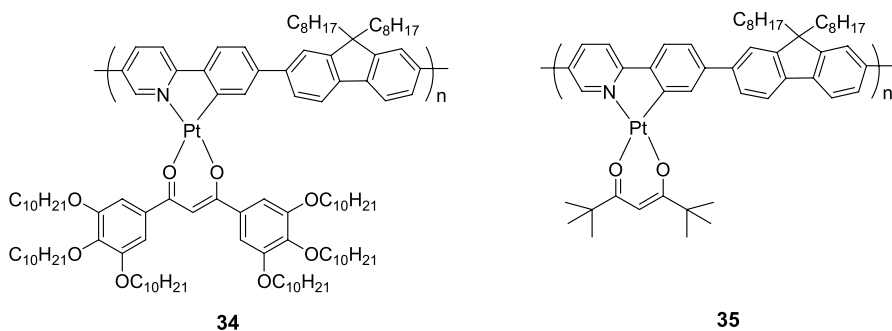


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Scheme 10 Chemical structure of polyfluorene derivatives with on-chain Pt(II) complexes showing molecular wire behavior

bridge, and Pt(II) tetraphenylporphyrin (PtTPP), in which the energy transfer is facilitated by energy alignment of the components (polymer 33). Alq₃- and fluorene fragments appear to form a single fluorophore owing to strong electronic coupling facilitating the singlet exciton migration to the porphyrin. The materials show effective singlet and triplet energy transfer, and exhibit red emission with high color purity.

The use of fluorescent conjugated polymers is an established method for achieving a large degree of amplification for the chemosensing of analytes in both solution and solid states. Swager et al. [57] have sought to investigate the potential of phosphorescent conjugated polymers as chemosensing materials. The longer lifetimes of triplet excitons in conjugated materials may lead to increased sensitivity to trace analytes. They synthesized copolymers (polymer 34 and 35) containing fluorene and cyclometalated square-planar platinum complex. The polymeric nature of this conjugated material gives a sensitivity improvement for dissolved oxygen quantification, demonstrating the potential usage of phosphorescent conjugated polymers as chemosensing materials.



Scheme 11 Chemical structures of polyfluorenes with on-chain Pt(II) complexes used in chemosensors

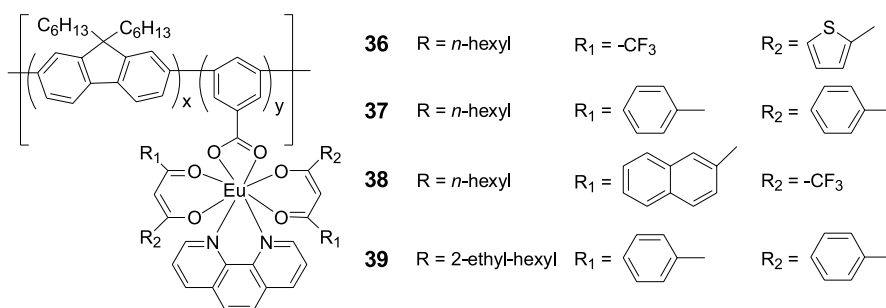
4

Polyfluorenes Containing Europium(III) Complexes

Rare earth compounds are excellent chromophores that exhibit intense emission with a narrow spectral bandwidth (full width at half-maximum of 5–20 nm) and relatively long decay lifetime (10^{-2} – 10^{-6} s) [58]. Since the emission from rare earth ions originates from transitions between the f levels of rare earth atom that are well protected from environmental perturbations by the filled $5s^2$ and $5p^6$ orbitals, the resulting emission spectra are expected to be sharp and narrow. They are the most widely used materials in inorganic light-emitting diodes [59]. A great deal of effort has also been devoted

to the application of rare earth complexes in organic memory devices and OLEDs [60].

Ling and his coworkers [61–64] designed and synthesized a series of conjugated copolymers (polymer 36–39) containing fluorene and Eu(III) complexes chelated to the main chains through a three-step process, involving Suzuki coupling copolymerization, hydrolysis of benzoate units, and postchelation. The photoluminescence spectra of the copolymer consisted of two emission bands, one in the 350–550 nm region and another at around 612 nm, corresponding to the $\pi^*-\pi$ transitions of the fluorene moieties and the $f-f$ transitions of the europium ions, respectively. In the copolymer films casting from solutions, emission from the fluorene moieties could be suppressed, and the absorbed excitation energy was transferred effectively to the Eu(III) complexes in the copolymer. Nearly monochromatic red emission was detected under UV excitation at room temperature.

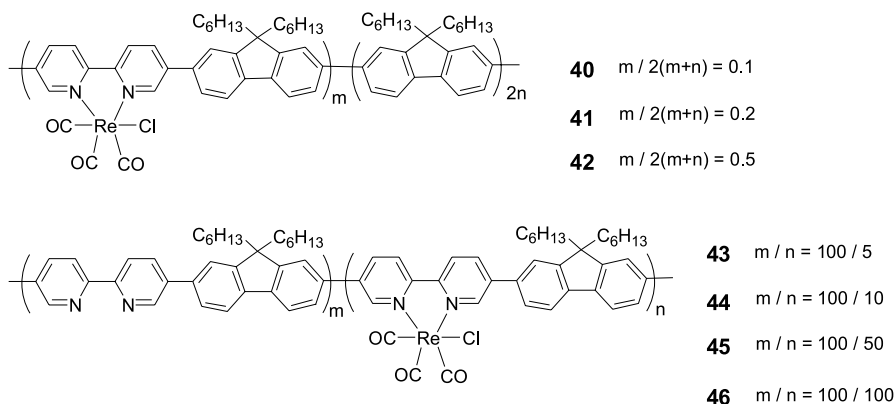


Scheme 12 Chemical structures of polyfluorenes with on-chain Eu(III) complexes

Subsequently, they first demonstrated a conjugated copolymer of 9,9-dialkylfluorene and Eu-complexed benzoate for write-once read-many-times (WORM) memory application in a sandwich structure of Al/polymer/ITO [65]. In these active polymers, the fluorene moiety served as the backbone and electron donor, while the europium complex served as the electron acceptor. An electrical bistability phenomenon was observed on this device: low conductivity state for the as-fabricated device and high conductivity state after device transition by applying a voltage. At the low conductivity state, the device showed a charge injection controlled current and at the high conductivity state, the device showed a space charge limited current. At the same applied voltage, the device exhibited two distinguishable conductivities. Thus, the device can be used as a WORM electronic memory, with a high ON/OFF current ratio up to 10^7 , stable ON-states and OFF-states up to 10^8 read cycles at a read voltage of 1 V, and projected stability up to 10 years at a constant voltage stress of 1 V.

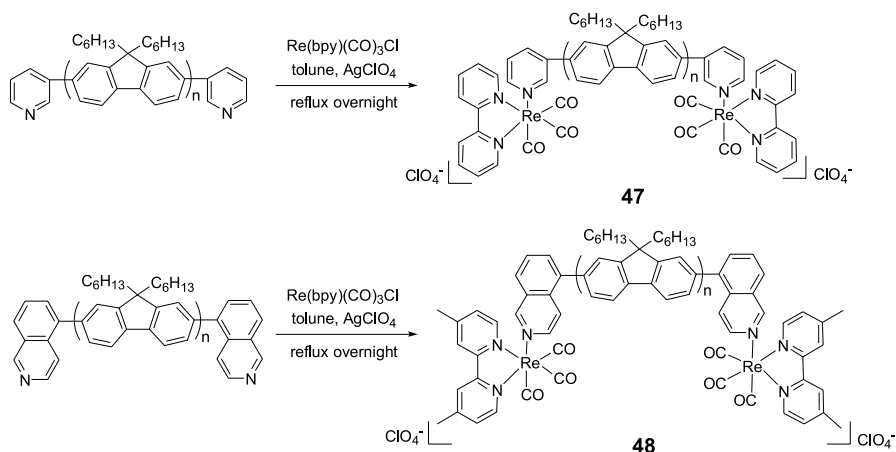
5 Polyfluorenes Containing Rhenium(I) or Ruthenium(II) Complexes

Complexes *fac*-(L)Re(I)(CO)₃Cl have attracted more and more attention due to the fact that *fac*-(L)Re-(I)(CO)₃Cl complexes are one of many typical metal-to-ligand charge-transfer (MLCT) materials with highly desirable properties, including microsecond excited-state lifetimes, intense visible absorption and emission, good redox chemistry properties, and high stability [66–69]. Interesting materials incorporating Re(I) complexes into π -conjugated polymer backbones have been reported [70–72]. Using 2,7-(9,9'-dihexylfluorene) and 2,2'-bipyridine (bpy) copolymers as the backbones, Ma et al. have synthesized a series of π -conjugated copolymers (polymer 40–46) incorporating (bpy)Re(CO)₃Cl in the backbones of the copolymers through a highly active replacement reaction of bpy elements and CO in Re(CO)₅Cl complexes [73]. They demonstrate that polymers incorporating metal complexes in the backbones may not be suitable for application in the OLEDs, but may be suitable for application in the photovoltaic fields. The incorporation of Re(I) into the polymer backbone results in the red shift of absorption and the presence of new peak at about 520 nm in emission spectra [74].



Scheme 13 Chemical structures of polyfluorenes with on-chain Re(I) complexes

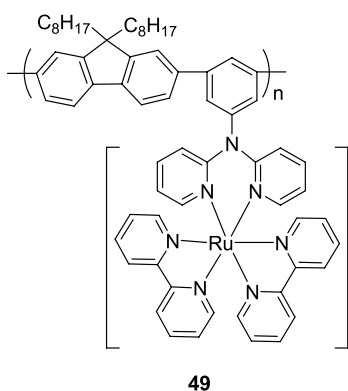
Hsu et al. [75, 76] reported a new method for incorporating metal complexes into polyfluorenes to prepare phosphorescent polymers (polymer 47 and 48). A pyridine end-capped polyfluorene has been synthesized. The pyridine was used to form a polymer metal complex with 2,2'-bipyridyl(tri-carbonyl)rhenium(I) chloride. Using the end-capping approach not only can control the molecular weight of polymer, but also avoid the interference of the metal complex and conjugated polymer in energy transfer. They can



Scheme 14 Synthesis of end-capped polyfluorenes with on-chain Re(I) complexes

change the end-capping monomers and the organic–metal complex to make differently colored phosphorescent polymers and even make a white-light phosphorescent polymer on a single polymer.

Polyfluorene with on-chain ruthenium complex (polymer **49**) has been synthesized by Suzuki polycondensation [77]. The photoluminescence of the copolymer was slightly blue-shifted as the concentration of dipyridylamine increased. The introduction of dipyridylamine and the ruthenium complex into the polymer significantly improved the photoluminescence efficiency.



Scheme 15 Chemical structure of polyfluorenes with on-chain Ru(II) complex

6 Conclusions and Outlook

In this review, the synthesis, properties, and applications in optoelectronic fields of polyfluorenes with on-chain metal centers have been briefly summarized. Metal complexes involving iridium(III), platinum(II), europium(III), rhenium(I), and ruthenium(II) complex coupled with polyfluorene are surveyed. Efficient energy transfer from polymer main-chain to metal-centers can occur in these host-guest systems. These kinds of novel polymers are usually applied in the fields of phosphorescent OLEDs, memory devices, and sensors. In particular, the realization of efficient energy transfer and phosphorescence offers a huge potential for future optoelectronic devices based on these kinds of materials.

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