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Phosphorescent polymer light-emitting diodes based on an end-capped polyfluorene with Rhenium (I) chromophores

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Abstract

A novel electrophosphorescent polymer was prepared by a pyridine end-capped polyfluorene reacted with 2,2-bipyridyl(tricarbonyl)rhenium(I) chloride. Using this approach, we can simultaneously control the molecular weight of the polymer, and incorporate phosphorescent metal complexes to the polymer without the phase separation problem between the metal and polymer. The incorporation of the metal complexes into the polymer has been demonstrated by utilizing ^{1}H-NMR, Ultraviolet-visible (UV–vis) spectroscopy, PL spectra and EL spectra.

Keywords: Phosphorescent; Light-emitting diodes; Rhenium complex

1. Introduction

Due to their high quantum efficiency, electrophosphorescent light-emitting diodes (LED) have attracted more and more attention recently. Both singlet and triplet excitons can be fully utilized in electrophosphorescence due to the strong spin-orbital coupling effect of heavy-metal ions in phosphorescent complexes. Therefore, a maximum 100% internal quantum efficiency can be achieved theoretically. Several researches have been reported about doping electrophosphorescent organic metals, such as iridium, ruthenium and rhenium, in organic light-emitting diodes (OLED) and polymer light-emitting diodes (PLED). The devices' efficiencies improved significantly [1–6] although there might have been a phase separation problem between the dopant and the polymers. Incorporating metal complexes into conjugated polymers backbones for use as phosphorescent polymer materials has also been reported. For example, rhenium was connected on the main-chain of polyfluorenes or iridium was attached on the side-chain of polyfluorenes [7–9]. Besides improving quantum efficiency, the organic metal complexes can also be used to tune the color of the LED.

In this work, we tried a new way to incorporate organic metals in polyfluorenes. A pyridine end-capped polyfluorene has been synthesized. The pyridine was used to form a polymer metal complex with 2,2-bipyridyl(tricarbonyl)rhenium(I) chloride. Using the end-capping approach can not only control the molecular weight of polymer, but also can avoid the interference of the organic metal complex and conjugated polymer in energy transfer.

2. Experimental

2.1. Materials

Toluene and *N*,*N*-dimethylformamide (DMF) were obtained from TEDIA, and distilled over calcium hydrate. Chloroform was also purchased from TEDIA. 2,7-Dibromo-9,9-dioctylfluore, 3-bromopyridine, 1,5-cyclooctadienene, 2,2-dipyridyl, Bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$], and poly(styrene sulfonic acid) doped poly(ethylenedioxythiophene) [PEDOT:PSS] were obtained from Aldrich. 2,2-Bipyridyl(tricarbonyl)rhenium(I) chloride[(bpy)Re(CO)$_3$Cl] was synthesized according to the literature procedure [6].

2.2. Instrumentation

^{1}HNMR spectra were collected on a Brucker Advance 600 spectrometer. Molecular weight determination was obtained by using a Waters GPC 2414 in tetrahydrofuran via a calibration

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curve of polystyrene standards. Ultraviolet-visible (UV–vis) absorption spectra were recorded on a Hitachi U-2001 spectrophotometer. Photoluminescent (PL) spectra were measured by a Hitachi F-4500 fluorescence spectrometer. Electroluminescent (EL) spectra of the devices were measured using a Photoresearch PR650. Cyclic voltammetry was carried out on a potentiostat/galvanostat model 283 (Princeton Applied Research) with a platinum electrode at a scan rate of 50 mV/s against Ag/AgCl reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN).

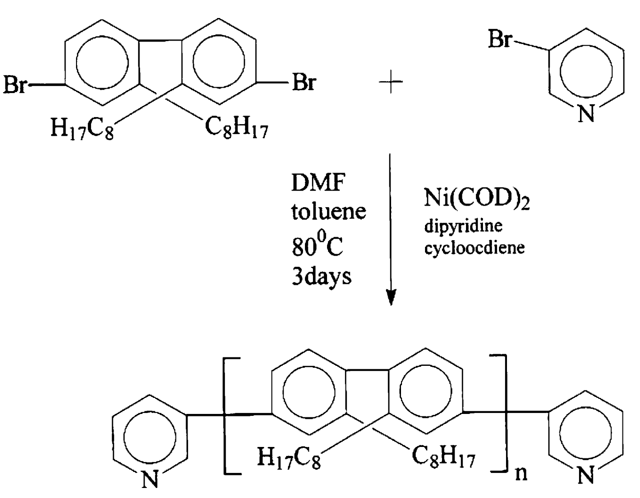
2.3. Synthesis of pyridine end-capped polyfluorene (PFO-endpy)

To a 100 mL round bottom flask, $Ni(COD)_2$ (2 g, 7.11 mmol), 2,2-dipyridyl (1.11 g, 7.11 mmol) and 1,5-cyclooctadiene (0.768 g, 7.11 mmol) were dissolved in 10 mL of DMF under a nitrogen atmosphere. The solution was heated to 80 °C for half an hour to form a purple complex. 2,7-Dibromo-9,9-dioctylfluorene (1.64 g, 3 mmol) and 3-bromopyridine (0.1 g, 0.6 mmol) in a mixture of toluene (30 mL) and DMF (5 mL) were added to the solution, and heated at 80 °C for another 3 days. After being cooled to room temperature, the reaction mixture was poured into a mixture of 200 mL of HC1, 200 mL of acetone and 200 mL of methanol, which was stirred for 2 h. The solid was filtered, and redissolved in chloroform. Then it was precipitated in a large amount of methanol. The pale yellow solid was dried in a vacuum oven at 60 °C for overnight to give 0.9 g of product (74% yield). The synthetic route is shown in Scheme 1.

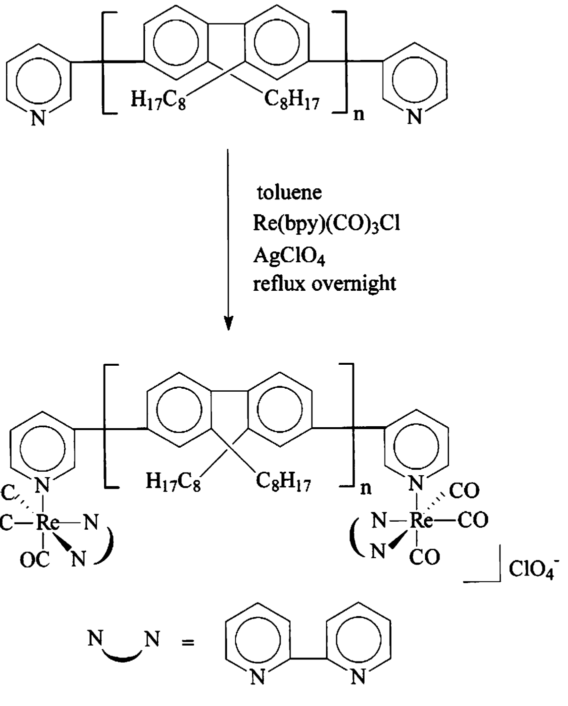
^{1}H-NMR (600 MHz, $CDCl_3$, ppm): 9.09(s, ArH), 8.68 (s, ArH), 7.99 (s, ArH), 7.93 (s, ArH), 7.83 (m, ArH), 7.68 (m, ArH), 2.12(t, 4H), 1.14 (m, 24H), 0.82(t, 6H). GPC (THF): Mn = 7073 g/mol, Mw = 13770 g/mol, PDI = 1.95.

2.4. Synthesis of polyfluorene rhenium complex (PF0-end2pyRe)

Under a nitrogen atmosphere, 50 mg of PFO-endpy was dissolved in 50 mL of toluene in a 100 mL round bottom flask, kept under dark. 2,2-Bipyridyl(tricarbonyl)rhenium(I) chloride (14 mg, 0.03 mmol) and silver perchlorate (10 mg, 0.05 mmol) were added consecutively to the reaction mixture, and the resulting solution was refluxed overnight. After being cooled to room temperature, the solution was filtered to get rid of AgCl. After evaporating the solvent, the polymer solid was redissolved in chloroform and then precipitated in a large amount of methanol. The polymer power was dried in vacuum at 60 °C overnight. The synthetic route is shown in Scheme 2.



Scheme 1. Synthesis of PFO-endpy.



Scheme 2. Synthesis of PFO-end2pyRe.

^{1}H-NMR (600 MHz, CDC1$_3$, ppm): 9.12 (s, ArH), 8.74 (d, ArH), 8.14 (s, ArH), 7.93 (d, ArH), 7.83 (m, ArH), 7.68 (m, ArH), 7.55 (d, ArH), 2.12 (t, 4H), 1.14 (m, 24H), 0.82 (t, 6H).

2.5. Light-emitting device fabrication

Patterned indium tin oxide (ITO) glasses were cleaned with acetone, 2-propanol and deionized water in an ultrasonic bath. A thin hole injection layer of poly(styrene sulfonic acid) doped poly(ethylenedioxythiophene) [PEDOT:PSS] was spin-coated on the ITO. On top of it, the emitting polymer was spin-coated from its solution in chloroform. Finally, the cathode Ca and Al were deposited by thermo-evaporation under a vacuum of 10^{-5} Torr.

3. Results and discussion

For polymers to be used in the fabrication of LED devices, the molecular weight of polymers is an important factor. If the molecular weight is too low, it is difficult to form a good film. On the other hand, if the molecular weight is too high, the polymers are hard to dissolve in the solvent. In this study, we used an end-capping reagent, 3-bromopyridine, to control the molecular