Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Synthetic Metals 153 (2005) 193–196

SYNTHETIC METALS

www.elsevier.com/locate/synmet

Synthesis and Electroluminescent Properties of Copolymers Derived from Fluorene and Metal-Free and Pt (II) Tetraphenylporphyrin

Q. Hou[a,b], Y. Zhang[a], R. Q. Yang[a], W. Yang[a], Y. Cao[a*]

[a] *Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Key Laboratory of Specially Functional Materials and Advanced Manufacturing Technology, Guangzhou 510640, China*

[b] *Department of Chemistry, South China Normal University, Guangzhou, 510630, China*

Abstract

A series of novel soluble conjugated copolymers derived from 9,9-dioctylfluorene (DOF) with metal-free and Pt (II) tetraphenylporphyrin (TPP) were synthesized via palladium-catalyzed Suzuki coupling reaction, with TPP content in the copolymers of 0.5%, 1%, 5%, 20% and 50% respectively. Platinum (II) (Pt) were incorporated into the copolymers by reaction of the copolymers with $PtCl_2$. Emission from DOF segment was completely quenched at very low metal-free TPP content (1%). The copolymers of DOF-co-TPP emit saturated red emission that is red-shifted slightly with increasing the TPP contents. After Introducing Pt, the emission peak of the copolymers is blue-shifted. Electroluminescent (EL) quantum efficiency of the devices based on the copolymers was 0.12% for copolymer with 5% TPP content and EL efficiency PFO-PtTPP was 0.15% for metal complex with 1% PtTPP content.

Keywords: Polyfluorene, Metal-Free Tetraphenylporphyrin, Pt (II)-Tetraphenylporphyrin, electroluminescence

1. Introduction

Many polyfluorenes (PF) and their derivatives have been studied since poly(9,9-di-n-hexylfluorene) (PDHF) was first reported by Yoshino et al. in 1989 [1]. Polyfluorenes have highly efficient fluorescent quantum yield and excellent thermal and oxidative stability, and can be easily processed into thin films through spin coating onto substrates from solution [2-5]. Emission color of poly- fluorenes can be tuned by using both polymer/polymer and dye/polymer blends or by copolymerization of fluorene with low band gap comonomers [6-8]. Porphyrin is one of the common red dyes, which has a good light, thermal and oxidative stability and show good fluorescence in solution [9]. Recently, there have been reports on the use of tetraphenylporphyrin (TPP) as guest blended into blue or green emitting polymer host to obtain red emitting diodes [10,11]. The use of metal-containing porphyrins in light-emitting diodes has also been reported [12,13]. However, these materials exhibit a tendency to aggregate and to self-quench their fluorescence. TPP as pendant groups attached to PPV polymer backbones with an alkylene spacer were investigated [14]. The syntheses and properties of bi- and trithiophenes which are covalently linked to metalated tetraphenylporphyrins via an oxaalkyl spacer were reported [15]. Star shaped porphyrins with four oligofluorene arms were reported [16]. Jiang, B. et al. have reported the conjugated polymers in which porphyrin units are linked by oligophenylenevinylenes of different, controllable lengths by use of Wittig reaction [17].

In this paper, TPP unit was introduced into the polyfluorene main chain in order to obtain red-emitting copolymers. We first report synthesis and characterization of copolymers derived from fluorene with TPP (structure in scheme 1) in less than or equal to 50% in the polymer composition by Suzuki coupling reaction. In this case, TPP and fluorene was bonded through conjugated chemical connections and each individual TPP unit is separated from both sides by polyfluorene segments. Platinum salts were reacted with the PFO-TPP copolymer to obtain metalated PFO-PtTPP copolymer. As a result, TPP unit is a part of conjugation of main chain. Upon excitation by UV light, photogenerated exitons at fluorene segment are quickly transferred to the TPP unit via intramolecular (also intermolecular) energy transfer. Copolymers emit exclusively red light characteristic of TPP unit. To the best of our knowledge, this is a first report which PtTPP (II) complexes were incorporated into conjugated polymer main chain via directly metallation of the conjugated metal-free copolymers by post-reaction of the TPP-containing copolymers with Pt salt. We expected that direct metallation of metal-free conjugated copolymers has certain advantages over the existed synthetic routes for

---

*Corresponding author. Tel: +86-20-87114609
Email: poycao@scut.edu.cn

doi:10.1016/j.synthmet.2005.07.287

preparation of copolymers containing metal-porphyrin complex in main chain. Synthesis, photo-physical and electroluminescent properties of metal-free and PtTPP (II) copolymers are reported and discussed.

2. Experimental

2.1. General

^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 500 or Bruker DRX 400 in deuterated chloroform solution. Number-average (*M*n) and weight-average (*M*w) molecular weights were determined by Waters GPC 2410 in THF using a calibration curve of polystyrene standards. The elemental analysis was performed on Vario EL Elemental Analysis Instrument (Elementar Co.). Platinum content in complex was tested on Z-5000 polarized Zeeman atomic absorption sepectrophotometer. UV-visible absorption spectra were recorded on a HP 8453 spectrophotometer. The PL quantum yields were determined in integrating sphere IS080 (Labsphere) with 325nm excitation of HeCd laser (Mells Griod). EL efficiency and brightness measurements were carried out with a calibrated silicon photodiode. EL spectra were determined by Instaspec 4 CCD spectrophotometer (Oriel.).

2.2. Materials

2,7-dibromo-9,9-dioctylfluorene(1), 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene(2) were prepared following the published procedures [18].

2.2.1 Synthesis of 2,13 (or 2,12)-Dibromotetraphenylporphyrin (3)

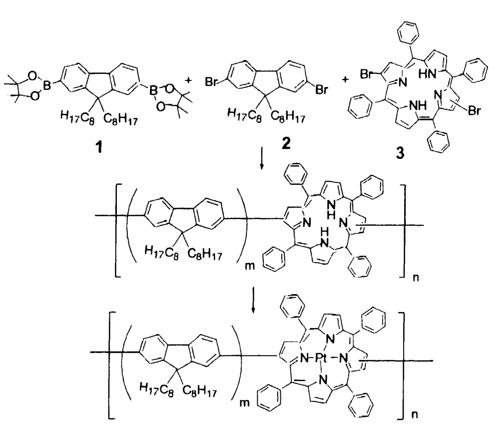
(3) was prepared following the published procedure [19,20]. NBS was added into the tetraphenylporphyrin solution in CHCl$_3$. The solution was refluxed 1h and cooled to room temperature. After a litter pyridine was added into the solution, the whole mixture was condensed and poured into methanol. The precipitated material was recovered by filtration through a funnel. The crude product was chromatographed twice on silica gel (eluent cyclohexane/benzene, 1:1) and further recrystallized from CH$_2$Cl$_2$/methanol gave the title compound (yield: 43%) as black solid. Element Anal. Calcd for $C_{44}H_{28}N_4Br_2$: C, 68.30%; H, 3.63%; N, 7.25%. Found: C, 68.08%; H, 3.86%; N, 6.98%. ^{1}H NMR (500MHz, CDCl$_3$, ppm): 8.91(2H), 8.84 (4H), 8.13 (8H), 7.76(4H), 7.74 (8H), -2.92 (2H). ^{13}C NMR (100MHz, CDCl$_3$, ppm): 134.55, 134.30, 128.86, 128.35, 128.07, 127.06, 126.79, 120.20.

2.2.2 Polymer Synthesis

All polymers were synthesized from 1, 2 and 3 via palladium catalyzed Suzuki coupling following the published procedure [18]. The resulting polymers were soluble in common organic solvents (toluene, chloroform, and tetrahydrofuran). The results of elemental analysis of nitrogen and carbon for each copolymer were used for calculation of actual copolymer composition. Element Anal. Found: for PFO-TPP0.5: C, 77.34%, N, <0.3%; PFO-TPP1: C, 88.16%; N, <0.3%; PFO-TPP5: C, 88.49%; N, 0.31%; PFO-TPP20: C, 87.60%; N, 2.33%; PFO-TPP50: C, 86.44%; N, 4.98%. PFO-TPP50: ^{1}H NMR (500MHz, CDCl$_3$, ppm): 8.84 (4H), 8.75(2H), 8.24(8H), 7.78(4H), 7.65(8H), 7.50(4H), 7.32(2H), 1.99 (4H), 1.25 (24H), 0.83 (6H), -2.54 (2H).

2.2.3 Synthesis of Pt (II) complex of copolymers PFO-TPP

After the PtCl$_2$ solution in benzonitrile was heated at 100℃ for 1h, the copolymer PFO-TPP solution in benzonitrile was added into the mixture and refluxed 10h. When cooled to room temperature, the mixture was poured into methanol and filtered. The crude product was chromatographed on siliga gel (toluene) and further purified from THF/methanol to give the Pt (II) complex of copolymer PFO-TPP. PFO-PtTPP50: ^{1}H NMR (500MHz, CDCl$_3$, ppm): 8.77(4H), 8.63(2H), 8.14(8H), 7.74 (12H), 7.51 (4H), 7.30 (2H), 1.96 (4H), 1.11 (24H), 0.85 (6H).



Scheme 1. Synthesis of copolymers of fluorene and TPP and their platinum (II) complexes

3. Results and Discussion

As can be seen from synthetic route in Scheme 1, conjugated copolymers of different compositions were prepared using palladium catalyzed Suzuki coupling methods. The actual composition of the TPP in the copolymer calculated from elemental analysis is slightly less than the feed ratio for PFO-TPP20 and 50, but substantially less (close to factor of 2) for PFO-TPP5 (Table 1). Both the low solubility of monomer TPP in toluene and the steric hindrance of benzene ring in TPP are probably responsible for the low TPP incorporation ratio. The number-average molecule weights (*Mn*) of the synthesized copolymers, as determined by gel permeation chromatography (GPC) using a polystyrene standard, were 6000 to 22000 with a polydispersity index (*Mw/Mn*) from 2.1 to 2.6.

Platinum (II) (Pt) was incorporated into TPP in the copolymer main chain by reaction of the metal-free

Table 1
Molecular Weights of the Copolymers and element analysis