ORGANIC LETTERS

2008
Vol. 10, No. 13
2913−2916

Synthesis, Structure, and Optoelectronic Properties of Phosphafluorene Copolymers

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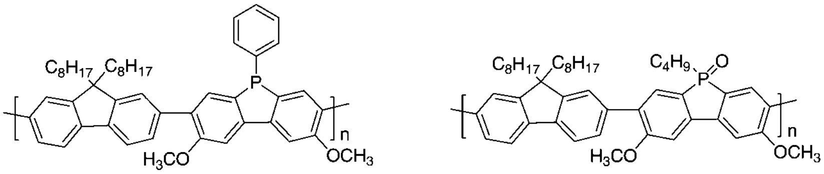
Received May 9, 2008

ABSTRACT



Copolymers of phosphafluorenes are obtained through Suzuki copolymerization. The phosphorus-containing copolymers show unique optical, electrochemical, and optoelectronic properties. Blue and white electroluminescence can be observed, depending on the modifications of the phosphorus atoms. It is the first time that conjugated polymers containing phosphafluorene have been prepared and used in PLEDs. Phosphafluorenes are new building blocks for conjugated oligomers and polymers.

Phosphorus has wide applications[1] in inorganic semiconductors, organic synthesis, catalysts, pesticides, and recently electronic and optoelectronic devices, functioning not only as ligands[2] for heavy-metal and rare-earth complexes, but also as materials[3] for light-emitting diodes. The incorporation of phosphorus moieties into conjugated molecules offers considerable promise for the development of new functional materials with novel properties because of the versatile reactivity and electronic properties of phosphorus centers.[4] The P−P skeleton is a powerful σ-scaffold to establish through-bond electronic interaction between π-chromophores with promising perspectives in optoelectronic applications. The phosphorus analogues of PPV have interesting electronic and spectroscopic properties.[5] The phosphorus-containing poly(*N*-arylaniline) copolymers are a new type of π-conjugated polymer with low oxidation potentials and electronic delocalization through phosphorus along the polymer chain.[6] Phosphole, the phosphorus analogue of pyrrole, displays a high potential for use in π-conjugated organic materials because of its favored exocyclic delocalization along the polymer chain.[7,8] The dithienophospholes have extraordinary optoelectronic properties, allowing for fine-tuning the electronic structure by simple chemical modifications and for its incorporation into the functional light-emitting diodes based on organophophorus materials.[9,10] These intriguing features of phosphorus-containing materials strongly support incorporating phosphorus atoms into conjugated molecules.

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10.1021/ol801068m CCC: $40.75

Among π-conjugated polymers, polyfluorenes (PFs) have many advantages[11] for polymeric light-emitting diodes (PLEDs). Polyfluorene-based Red, Green, and Blue materials for PLEDs have been realized.[12] However, PFs often show a tailed emission band at long wavelengths[13] in solid states and devices, leading to color instability. The polysilafluorenes[14,15] formed by replacing the vulnerable C-9 carbons in PFs with silicon atom has strong blue electroluminesence (EL) with high thermal and optical stabilities. The phosphorus analogue of fluorene and silafluorene (phosphafluorene) has been used in asymmetric catalysis,[16] and unsymmetrical 9-phosphafluorene oxides are of interest for P-chiral liquid crystals.[17] However, the applications of phosphafluorene in luminescence devices have not been found in the literature so far. The chemical and electronic configuration[18] of phosphafluorene is also very similar to that of carbazoles (nitrogenafluorenes) which are currently the core-building units for light-emitting materials and hole transporting materials.[19] It is interesting to investigate the optical and electronic properties of phosphafluorene, in which the phosphorus atom is in the same subgroup as nitrogen.[18]

In this Letter, we successfully synthesized copolymers of phosphafluorene (dibenzophosphole) and fluorene via Suzuki polymerization, and the optoelectronic properties of the polymers were investigated. In contrast to the polysilafluorenes which emit only blue light as polyfluorene, the prepared phosphafluorene-containing copolymers show not only strong blue light emitting but also single layer white EL. It is surprising that the oxidized phosphorus atom on phosphafluorene significantly changed the blue EL of polyfluorene into white, although the actual incorporation ratio of phosphafluorene oxide is only 11% revealed by HNMR. The extraordinary optical and electronic features of phosphafluorene suggest its great potential in opto and electro devices and applications.

Suzuki coupling polycondensation between the comonomers of **I**/**II**, **III**, and **IV**[20,21] shown in Scheme 1 afforded the copolymers identified as PFO-PhPF10 and PFO-BuPFO10, respectively, in which PFO is poly[2,7-(9,9-dioctylfluorene)], PhPF is 3,6-dimethoxyl-9-phenyl-9-phosphafluorene, BuPFO is 3,6-dimethoxyl-9-butyl-9-phosphafluorene oxide, and the feed content is 10 mol %. The number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PI = M_w/M_n) of the copolymers determined by gel permeation chromatography (GPC) with polystyrene standards are listed in Table 1. The lower molecular weight of PFO-BuPFO10 is probably due to the harmful interactions between the Pd catalyst and BuPFO, resulting in reduced catalyst efficiency.[22] The large polydispersity of the molecular weight of PFO-PhF10 may also be due to the interactions between the Pd catalyst and PhPF, which has a similar structure of

Scheme 1. Synthesis of Phosphafluorene Copolymers

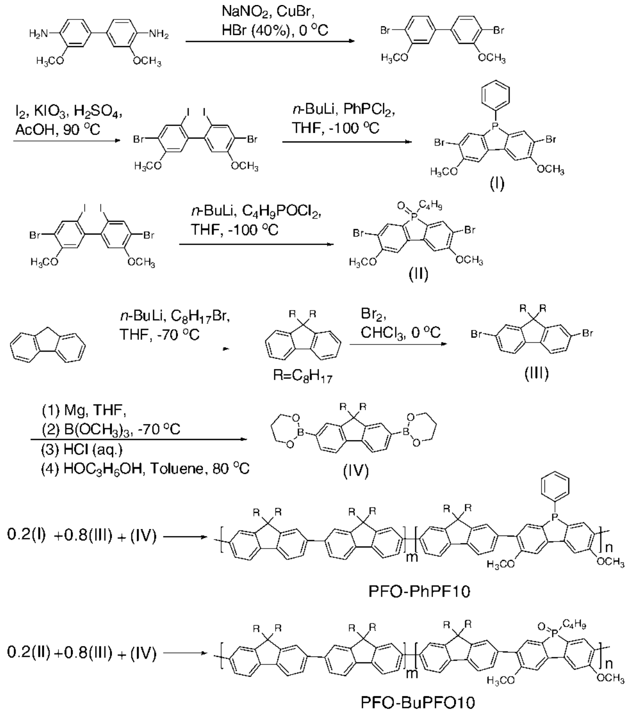

Table 1. Composition, Number-Average (M_n) and Weight-Average (M_w) Molecular Weight, Polydispersity Index (M_w/M_n), and Thermal Properties of Phosphafluorene Copolymers[a]

polymer[b]	composition[c]/ %	M_n	M_w	M_w/M_n	T_g/°C	T_d/°C
PFO		14 000	20 000	1.4	78	426
PFO-PhPF10	7	15 400	35 800	2.3	81	403
PFO-BuPFO10	11	9 500	10 200	1.1	52	403

[a] Measured by GPC, using polystyrene as standard. [b] The mol feed content of phosphafluorenes is 10%. [c] The mol content of the phosphafluorene unit in polymers is calculated via ^{1}H NMR.

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Table 2. The Optical and Electrochemical Properties of the Phosphafluorene Copolymers

polymer	λ_{max}/solution (nm) abs.	λ_{max}/solution (nm) em.	λ_{max}/film (nm) abs.	λ_{max}/film (nm) em.	E_{op}[a] (eV)	HOMO/LUMO (eV)	QE[b] (%)
PFO	383	420, 438 (475)	391	438, 468 (495)	2.84	−5.84/−2.16	59.1
PFO-PhPF10	384	418, 442 (472)	393, 429	438, 462 (492)	2.81	−5.87/−2.19	53.1
PFO-BuPFO10	387	418, 442 (472)	402, 430	441, 462, 492	2.74	−/−	52.4

[a] Optical bandgap (E_{op}) calculated from the onset of absorption spectra of the solid film. [b] Absolute PL quantum yield (QE) measured in the integrating sphere.

triphenylphosphine. The Suzuki polymerization conditions for phosphafluorenes need to be optimized and investigated at the mechanism level.[23]

The chemical structure of the copolymers was verified by ^{1}H NMR spectra. The NMR signal of methoxyl around 4.05 ppm was considered as a chemical structure probe of phosphafluorene units.[24] From this useful probe, the PhPF10 and BuPFO composition in the copolymer was calculated to be 7 and 11 mol %, respectively, suggesting the copolymerization reactivity of the comonomers decreases in the following order: BuPFO > fluorene > PhPF. The much lower copolymerization ability of the dibromated PhPF than that of BuPFO is probably due to the bulkier substituent of phenyl and its lower solubility in the copolymerization medium. The slightly higher actual content of BuPFO than its feed content suggests that the copolymerization ability of dibromated BuPFO is higher than that of dibromofluorene although the spatial hindrance of methoxyl substituents beside the polymerization sites may hinder the process of Suzuki polymerization.[24] The quite different copolymerization behavior of the phosphafluorenes indicates the great tuning ability by chemical modifications of the phosphorus center.[15]

The copolymers have good solubility in chloroform, tetrahydrofuran, and other common organic solvents and uniform thin films can be cast from the solutions. The starting temperatures of thermal decomposition (T_d) of the copolymers measured by thermogravimetric analysis (TGA) are both higher than 403 °C in nitrogen. The glass transition temperatures (T_g) of PFO-PhPF10 and PFO-BuPFO10 were determined to be around 81 and 52 °C, respectively, according to differential scanning calorimetry (DSC). The low T_g of PFO-BuPFO10 may be due to the flexible butyl substitutes and its lower molecular weight.

From Figure 1a, PFO-PhPF10 and PFO-BuPFO10 display PFO-segment-dominated[25] absorption and emission spectra in THF (see Table 2) with slightly red-shifted main absorption peak at 384 and 387 nm, respectively, in comparison with that of PFO, and with strong photoluminescence (PL) emission peaks around 418, 441, and 472 nm, indicating that the phosphafluorene incorporation does not result in conjugation breakage of the PFO chain. The separate absorption and emission of phosphafluorene units cannot be observed since phosphafluorene has similar poly-*p*-phenylene backbone chromophores as PFs.[18]

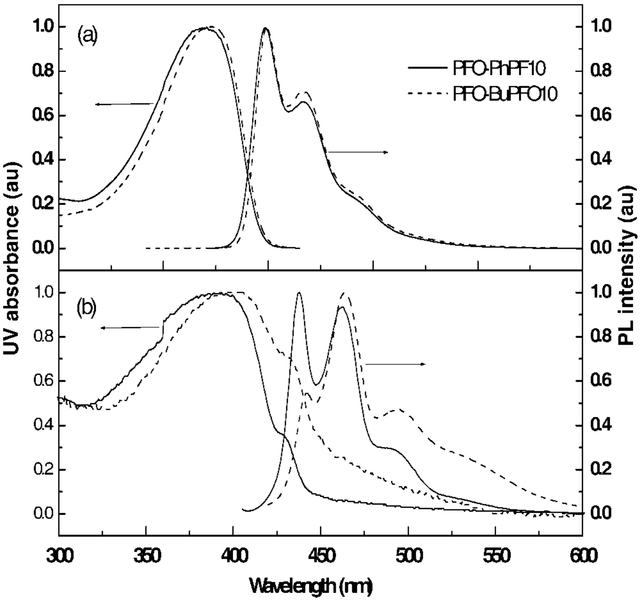

Figure 1. Absorption (UV) and fluorescence (PL) spectra of PFO-PhPF10 and PFO-BuPFO10 in dilute THF solution (a) and in thin film (b).

The absorption spectra of PFO-PhPF10 and PFO-BuPFO10 in cast film (see Figure 1b) show peaks at 393 and 402 nm, respectively, and shoulders around 430 nm. The red-shifted absoption peaks in comparison with that of PFO (391 nm)[26] suggest that conjugated length in the solid state increases after phosphafluorene incorporation and BuPFO has greater effects than PhPF. The additional absorption shoulder around 430 nm is related to the β-phase,[27] indicating that phosphafluorene incorporation increases intrachain order. The emission specta are remarkably similar to that of PFO (β-phase) but with enhanced 0−1 transition (462 nm) especially

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for PFO-BuPFO10, showing that phosphafluorene units make the polymer more ordered (β-phase) and hinder the exiton migration to lowest energy gap segments (0−0 transition).[26] The oxidation of the phosphorus center results in the red-shift of the absorption and emission peaks, which is also observed in phosphole and bisthienylphosphole systems.[4] The optical bandgap calculated from the onset of absorption spectra of the polymeric solid film decreases with the introduction of the phosphafluorene unit into PFO, suggesting that the phosphafluorene incorporation leads to increased conjugation length despite the spacial hindrance of the methoxyl substituents of phosphafluorene units which will lead to shorter conjugation length. The oxidation of the phosphorus center results in a decreased energy bandgap.[4] High photoluminescence efficiency was observed for PFO-PhPF10 and PFO-BuPFO10 with the absolute quantum efficiency (QE) of 53.1% and 52.4% respectively. The small incorporation ratio of phosphafluorene into PFO significantly changes the photophysical properties of PFO in the solid state, while in the dilute THF solution the UV and PL spectra remain identical with those of PFO. It seems that phosphafluorene units influence the photophysical properties mainly through interchain interactions.

PFO-PhPF10 has reversible electrochemical redox behavior as indicated by cyclic voltammetry (CV), while PFO-BuPFO10s CV is irreversible. From the onset potential of electrochemical reduction and oxidation, LUMO and HOMO of PFO-PhPF10 were calculated to be −5.87 and −2.19 eV, respectively. The incorporation of phosphafluorene into PFO results in decreased HOMO, decreased LUMO, and unchanged energy gap (ΔE), indicating improved electron injection and transport ability of the copolymer. The copolymer even has slightly lower LUMO than that of polysilafluorene (−2.18 eV),[14] suggesting the much greater impact of phosphorus than that of silicon and comparative electron injection and transfer properties of PFO-PhPF10 in comparison with those of polysilafluorenes.

Preliminary results for the EL emission spectra of PFO, PFO-PhPF10, and PFO-BuPFO10 (see Figure 2) were measured on a single layer device in the configuration ITO/PEDOT/polymer/Ba/Al. PFO-PhPF10 showed a blue EL (CIE = 0.21, 0.24) with emission maxima at 424, 450, and 478 nm, while the EL of PFO-BuPFO10 is very different and shows white-light emission (CIE = 0.34, 0.36). The maximum luminescent brightness of PFO-PhPF10 is 1423 cd/m^2, which is much higher than the 142 cd/m^2 of PFO-BuPFO10 in the same device configuration. The EL spectrum of PFO-PhPF10 is blue-shifted in comparison with that of PFO with lower brightness. The interesting EL spectra of phosphafluorene-incorporated copolymers show not only their great potential as blue light-emitting and single-layer white EL materials, but also the great property adjustability of the small ratio incorporated phosphafluorene units through the phosphorus atom modifications. The high impact of the phosphafluroenes on their EL spectra needs to be further investigated.

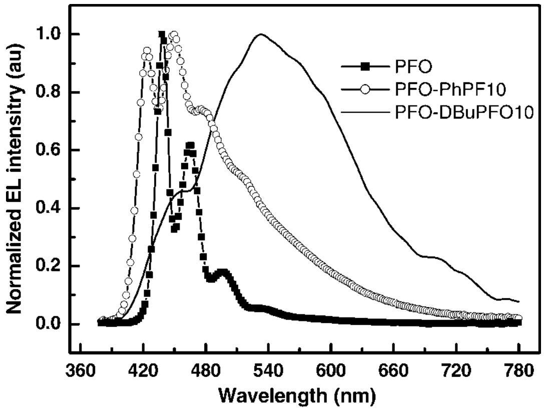

Figure 2. Electroluminescence (EL) spectra of the phosphafluorene copolymers with the following device configuration: ITO/PEDOT/polymer/Ba/Al.

In conclusion, we successfully synthesized new phosphorus-containing copolymers based on phosphafluorene and fluorene units. The influence of phosphafluorenes on polymerization reaction, thermoproperties, and photophysical, electrochemical, and electroluminesent properties was investigated. It is the first time that conjugated polymers containing phosphafluorene have been prepared and used in PLEDs. The PFO-PhPF10 and PFO-BuPFO10 show unique optical, electrochemical, and optoelectronic properties. The chemical modifications of the phosphorus atom of 11 mol % phosphafluorene in the copolymer significantly changed the properties of the polymer, and tuned the blue EL into a white one. The successful synthesis and the studies of the solution-processable phosphafluorene−fluorene conjugated copolymers indicate that the 2,7-functionalized phosphafluorene is a new building block for conjugated polymers with strong blue light-emitting and single-layer white EL. The further optimization of the materials is to prepare a higher content of phosphafluorene units and their homopolymers as well as oligomers. The development of new functional devices based on the phosphafluorene π-conjugated materials is currently underway in our laboratory.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China under Grants 20774043, 20574012, and 90406021, the Fok Ying Tung Education Foundation under Grants 111051 as well as the Nanjing University of Posts and Telecommunications (NUPT) under Grant NY206073.

Supporting Information Available: Experimental procedures, spectroscopic data, and NMR spectra for new compounds and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

OL801068M