

Highly sensitive triphenylamine-based fluorescent chemosensors for metal ions

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國科會計畫編號：NSC 99-2113-M-155-001

Abstract

Two terpyridine-containing conjugated polymers (PFT and HPFT) have been synthesized using Suzuki coupling polymerization and their photophysical and chemosensory properties have been investigated in this work. Both PFT and HPFT exhibit favorable thermal stabilities, with thermal decomposition temperatures greater than 406.7 °C. Increasing the polarity of organic solvents produces bathochromic shifts in the PL spectra of PFT and HPFT. PFT and HPFT containing pendant terpyridyl groups exhibit increased sensitivity to the Ni²⁺ ion, with Stern-Volmer constants (K_{sv}) of $1.86 \times 10^4 \text{ M}^{-1}$ and $5.01 \times 10^4 \text{ M}^{-1}$, respectively. Our results suggest that HPFT is a promising material for chemosensory applications.

本研究利用 Suzuki 耦合聚合法合成兩種含有吡啶基團的共軛高分子(PFT 和 HPFT)，探討其光物理特性和螢光化學感應性質。PFT 和 HPFT 均呈現高熱穩定性，熱裂解溫度都大於 406.7 度。經由不同極性有機溶劑分析之下，兩者的發光波長均隨著溶劑極性的增加，呈現紅位移的現象。含有末端吡啶基團的 PFT 和 HPFT 均對於鎳離子有高度的靈敏性，線性 PFT 的 K_{sv} 常數為 $1.86 \times 10^4 \text{ M}^{-1}$ ，超分枝狀 HPFT 的 K_{sv} 常數為 $5.01 \times 10^4 \text{ M}^{-1}$ ，超分枝狀 HPFT 在螢光感測應用上展現優異性能。

Keywords: conjugated polymer; chemosensor; triphenylamine; hyperbranched

INTRODUCTION

The application of fluorescent conjugated polymers as versatile sensory materials has proven particularly attractive for environmental applications during the past decade because of their high analyte sensitivity and ease of measurement [1-4]. Recently, fluorescent chemosensors based on conjugated polymers have been developed that can be used to measure pH and can detect metal ions and biological species. These detection properties arise because the fluorescence properties of the chemosensor are dependent on coupling between receptors on the polymer and the detected analytes [5].

In this study, we used a palladium-catalyzed Suzuki coupling reaction to synthesize a novel hyperbranched oligofluorene (HPFT) with two carbazole groups as branching points, and with terpyridine pendant ligands. We examined the effects of the hyperbranched structure on the optical properties of the conjugated polymers, and the effects of terpyridyl substitution on the sensory characteristics of the fluorescent chemosensors. Our results showed HPFT shows high potential for application in optoelectronic devices such as hole-injection materials in PLEDs, and sensing materials in chemosensors.

EXPERIMENTAL

Synthesis of polymers

Poly(9,9-dihexylfluorene) (PF) was synthesized by our laboratory and was synthesized by the published procedures [6-7]. The general synthetic procedures for the polyfluorene derivatives are described as follows: To a solution of predetermined amount monomers in toluene was added with aqueous potassium carbonate (2M) and ethanol. The mixture was degassed and exchanged with nitrogen for three times, and a catalytic amount of tetrakis(triphenylphosphine) palladium [Pd(PPh₃)₄] (1.5 mol %) was added in one portion under nitrogen atmosphere. The solution was then stirred at 80 °C under nitrogen atmosphere. After stirring for 24 h, the solution was poured into a large amount of methanol solution, and then the crude polymers were collected by filtration and further purified by extraction with acetone for 24 h in a Soxhlet apparatus to remove monomers and catalyst residues.

Yield of PFT: 24.5 %. $T_g = 132.5$ °C. FTIR (KBr pellet, $\nu_{\max}/\text{cm}^{-1}$): 2925, 2865 (C-H), 1590, 1487 (C-C in Ar). ¹H-NMR (CDCl₃, δ in ppm): 0.81-0.86 (m, CH₃), 1.11-1.23 (m, CH₂), 2.02-2.15 (m, CH₂), 7.18-7.86 (m, Ar-H), 8.60-8.80 (m, Ar-H). Anal. Calcd. (%) from feed: C, 87.99; H, 6.20; N, 4.51. Found: C, 86.24; H, 6.56; N, 3.84.

Yield of HPFT: 16.7 %. $T_g = 115.2$ °C. FTIR (KBr pellet, $\nu_{\max}/\text{cm}^{-1}$): 2924, 2840 (C-H), 1582, 1465 (C-C in Ar). $^1\text{H-NMR}$ (CDCl_3 , δ in ppm): 0.61-0.86 (m, CH_3), 1.01-1.33 (m, CH_2), 1.91-2.15 (m, CH_2), 3.65-3.80 (m, CH_2) 7.18-7.86 (m, Ar-H), 8.61-8.79 (m, Ar-H). Anal. Found: C, 87.64; H, 6.93.

Fluorescent titration of polymer

Fluorescent titration experiments were carried out in THF solution. The chloride salts of Li^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Zn^{2+} , Ni^{2+} , Fe^{3+} , Ag^+ , Al^{3+} , Ba^{2+} , and Pb^{2+} (5.5×10^{-5} M) were dissolved in distilled water. Titration was done by adding the metal ion solution to a test tube with polymer solution. The final concentration of polymer was 1×10^{-6} M. Titration of the metal ions was terminated until no change in the fluorescence intensity was observed. The Stern-Volmer constant (K_{sv}) was estimated according to following equation:

$$(I_0/I) = 1 + K_{sv}[Q] \quad (1)$$

where I_0 and I are the intensity of PL spectrum without and with a quencher, respectively, K_{sv} is the Stern-Volmer constant (quenching coefficient), and $[Q]$ is the concentration of the quencher ions.

RESULTS AND DISCUSSION

Photophysical properties

Fig. 2 shows the absorption and photoluminescence (PL) spectra of the three polymers in toluene solutions and as films. The polymers exhibit strong UV-vis absorption bands at 380–387 nm in the toluene solution, resulting from π - π^* electronic transition within the polymer backbone. The electronic transition in PFT involves the migration of electron density from triphenylamine and fluorene donor groups toward the terpyridine acceptor, resulting in the observed intramolecular charge transfer (ICT) interactions and bathochromic shifts [8]. However, the PFT absorption band is red-shifted by approximately 6 nm relative to PF, and appears at 386 nm. The small shift in the PFT absorption band is a result of the low molecular weight of PFT and the presence of twisted and bulky triphenylamine groups in the polymer backbone. The triphenylamine groups induce conformational distortion and reduce the effective conjugation length of the polyfluorene chains [9-10].

In solution, the emission spectra of PF, PFT, and HPFT have maxima at 416, 462, and 466 nm (Fig. 2a), respectively. Compared with their solution spectra, the PL spectra of the three polymers in film state are red-shifted by approximately 8, 20, and 5 nm, respectively (Fig. 2b), implying that aggregation and the formation of excimers occur in the film state. The PL spectral red-shift of PFT (20 nm) in moving from the

solution to the film state is greater than that seen for HPFT (5 nm) because of the stronger interchain interactions that occur in PFT, which are caused by its linear structure. However, the smaller red-shift seen for hyperbranched HPFT mainly results from its branched and globular molecular structure.

Ion responsive properties

Fig. 3 shows the effect of complexation with various metal ions on the PL spectra of PFT and HPFT in a THF/H₂O solution. Adding Fe³⁺, Ni²⁺, Zn²⁺, Mn²⁺, or Ag⁺ to the solution results in a significant decrease in PL intensity, indicating that these cations provide efficient fluorescence quenching of the conjugated chain. In particular, the linear polymer PFT is quenched completely by Fe³⁺ and Ni²⁺ ions, indicating its high selectivity toward these two cations, whereas the hyperbranched polymer HPFT exhibits different chelating abilities that vary with the metal ion. HPFT is only quenched completely by the Ni²⁺ ion. Moreover, HPFT shows poor selectivity for the Fe³⁺ ion. Our results suggest the hyperbranched structures play a dominant role for HPFT in its high selectivity toward Ni²⁺. It also indicates that the incorporation of a strongly electron-donating carbazole moiety into the polymer chain changes the electron density in the polymer backbone. Therefore, the photoelectron energy transferring from the backbone to the terpyridine-metal complex in HPFT between backbones would be altered. This results in differences in coordination between metal ions and the terpyridyl receptors.

In the presence of Ca²⁺, Li⁺, Mg²⁺, Al³⁺, Ba²⁺, and Pb²⁺, the PL spectra of both PFT and HPFT show slight decreases in PL intensity. Complexation of metal ions does not induce any shift in the emission peak. The fluorescence color response to the different metal ions was highly visible. We attributed the fluorescence quenching behavior to strong cation binding between metal ions and the terpyridyl chelating groups, which facilitates the photoexcited energy transfer from the polymer backbone. Consequently, the small diameters and large charges of Fe³⁺ (1.28 Å, 1.83) and Ni²⁺ (1.44 Å, 1.91) ions might play important roles in determining their coordination strength with terpyridine groups.

CONCLUSIONS

We synthesized and characterized two triphenylamine-based PFs by using Suzuki coupling reactions. **PFT** and **HPFT** underwent an internal charge transfer after excitation, which resulted in solvatochromic behaviors; the resultant highly polar charge-separated emission state was effectively stabilized by polar solvents. **PFT** and **HPFT** exhibited high selectivity toward the Ni²⁺ ion, and the corresponding Stern-Volmer constants are $1.86 \times 10^4 \text{ M}^{-1}$ and $5.01 \times 10^4 \text{ M}^{-1}$. These results suggest

that HPFT containing the terpyridyl group is a promising chemosensory material.

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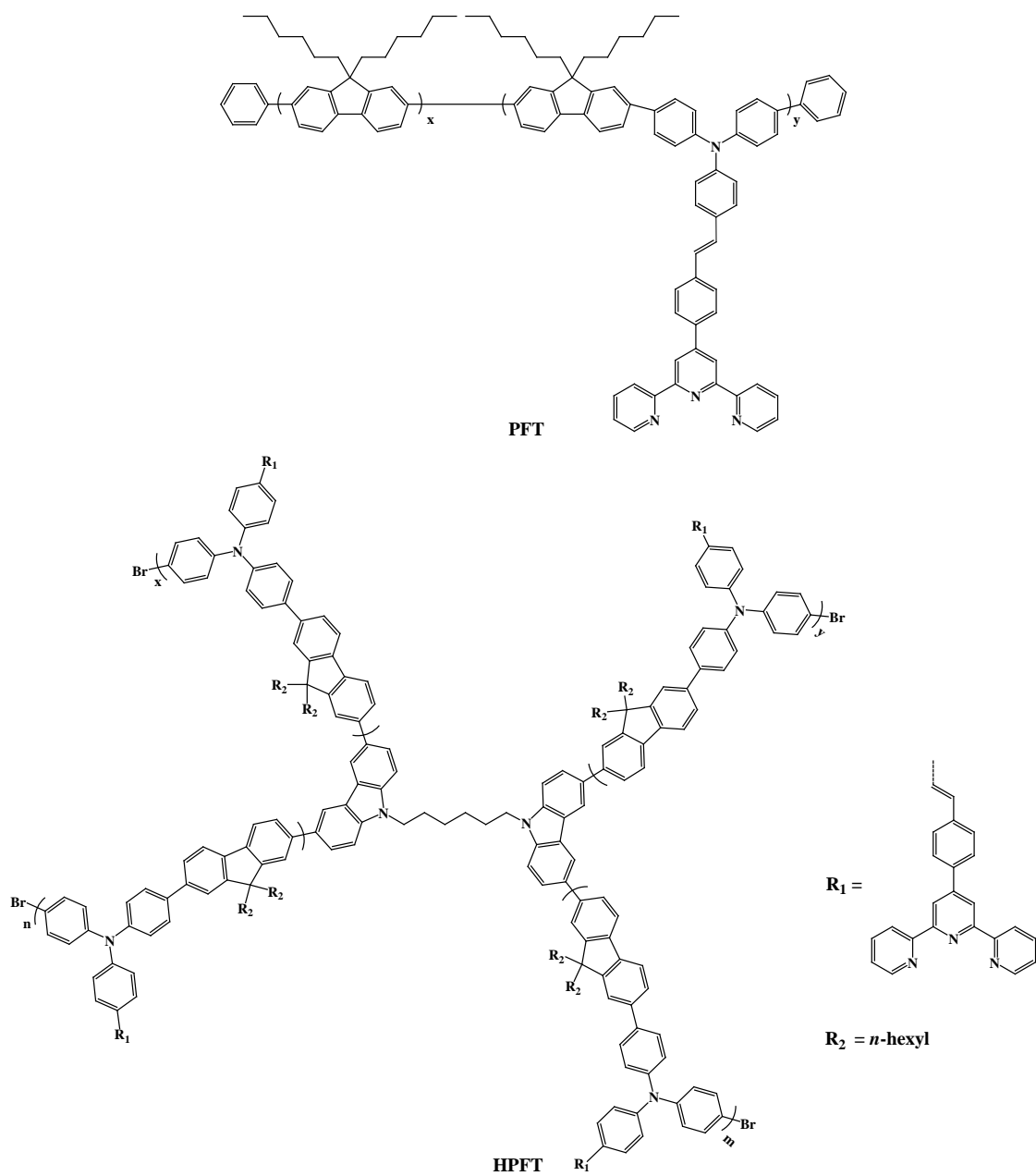


Figure 1. Chemical structures of PFT and HPFT.

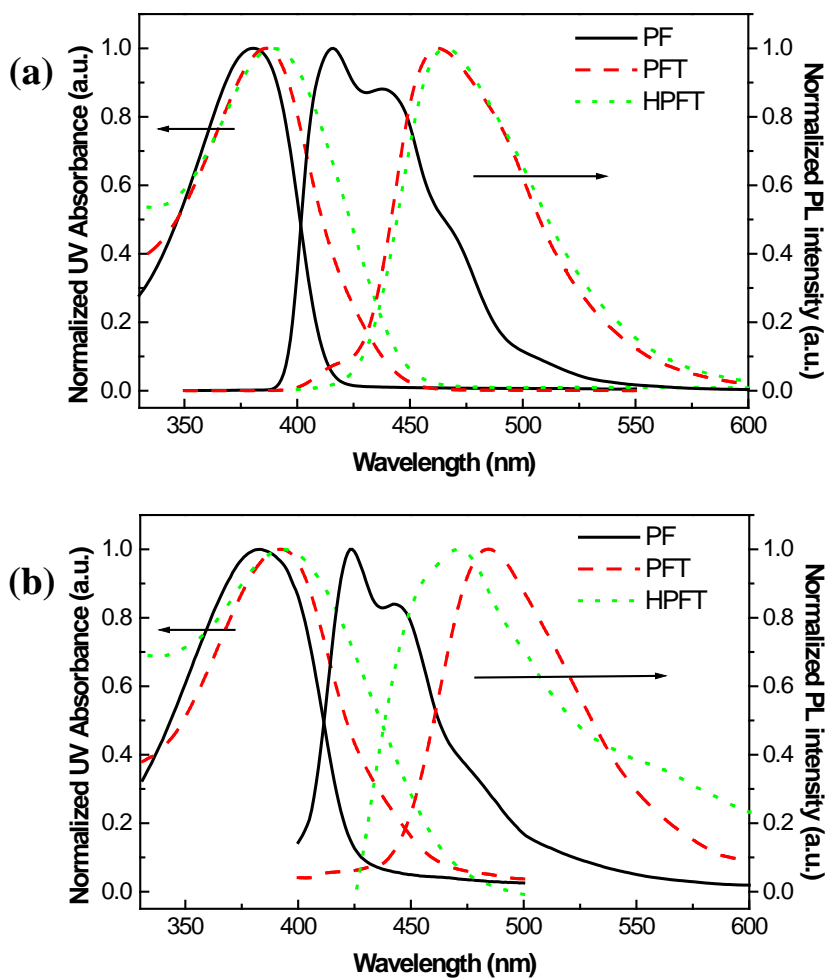


Figure 2. Normalized UV-visible absorption and PL spectra of polymers (a) in toluene solution and (b) in thin films.

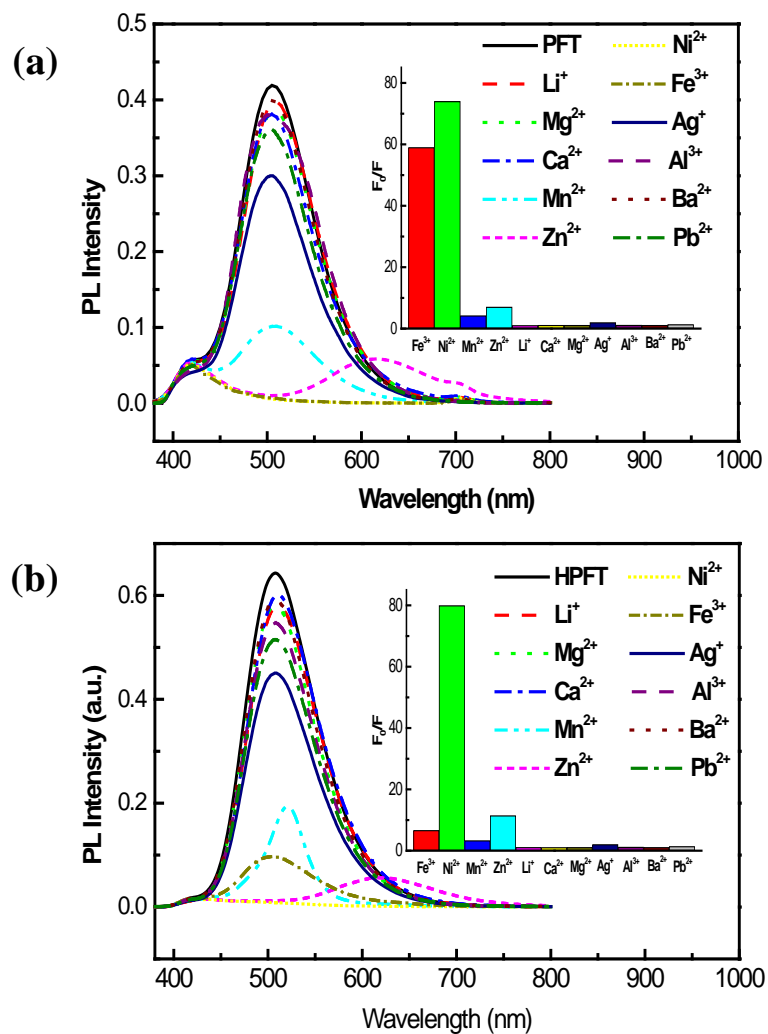


Figure 3. Photoluminescence spectra of (a) PFT and (b) HPFT in the presence of various metal ions (excitation: 385 nm). Concentration of polymer: 10^{-6} M in THF, concentration of metal ions: 5.5×10^{-5} M. Inset: PL response profiles for polymers by adding various metal ions in THF.