



# Conjugated polymers based on poly(fluorenylene ethynylene)s: Syntheses and sensing performance for nitroaromatics



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## ABSTRACT

Four conjugated polymers ( $P_1$ ,  $P_2$ ,  $P_3$  and  $P_4$ ) based on poly(fluorenylene ethynylene)s (PFEs) have been synthesized by introducing 9,9-diphenylfluorene units and/or thiophene units into the backbone of PFEs. These exotic units remarkably change the behaviors of polymer, such as the solubility, the peak wavelengths of the optical spectra, and the spectral red-shift of solid polymers, etc. As sensing materials for detecting nitroaromatics, all the four polymers show observable fluorescence quenching when DNT exists. For example, in DNT/THF solution, the quenching efficiencies ( $\eta_{EP}$ ) of  $P_2$  and  $P_4$  are 95% and 90% at quenching equilibrium respectively, which are much higher than those of  $P_1$  (77%) and  $P_3$  (72%). The high  $\eta_{EP}$  of  $P_2$  and  $P_4$  may be ascribed to the electron-rich character of thiophenylene units which can facilitate the electron-transfer between polymer and DNT. However, in another case of polymer films in DNT vapor,  $P_3$  shows higher quenching efficiency even than  $P_2$  at quenching equilibrium, which may be attributed to the fact that the steric hinderance of 9,9-diphenylfluorene units in  $P_3$  can improve the permeability of the film sensor.  $P_4$ , which contains both thiophenylene and 9,9-diphenylfluorene units, shows the highest quenching efficiency of 91% in DNT vapor at quenching equilibrium.

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## 1. Introduction

Conjugated polymers (CPs), which allow rapid propagation of exciton along the backbone due to the molecular wire effect, exhibit signal amplification effect when they serve as sensing materials [1–5]. The conceptual underpinnings in this field began with the work reported by Swager et al. (1995), in which the significantly amplified fluorescence quenching was demonstrated in a CPs sensor for detecting paraquat [6–8]. Since then, many CPs have been studied for detecting various analytes, especially for nitroaromatic compounds (NACs) [9–14]. However, CPs are inclined to self-aggregate into solid by  $\pi$ – $\pi$  stacking interaction between polymer backbones [15]. This kind of aggregation leads to two disadvantages which limit their application in chemical sensors: one is the fluorescence self-quenching induced by the energy migration between the polymer backbones; the other is the poor solubility for CPs in common solvents which mean bad processibility. Many strategies [16–20] have been used to prevent  $\pi$ – $\pi$  stacking interaction. For instance, Toal and Trogler incorporated rigid three-dimensional pentiptycene moieties into the backbone of poly(phenyleneethynylene), while Nie et al. and Leng et al. attached tetra-phenylmethyl as bulky side

blocks into the polycarbazolyene backbone. These studies demonstrated that the bulky rigid group can not only reduce  $\pi$ – $\pi$  stacking, but also enhance the permeability of the materials which facilitates the diffusion of analytes within the materials.

The fluorescence quenching of CPs to nitroaromatics is generally achieved by the electron-transfer donor–acceptor mechanism, in which the electron-deficient NACs act as electron acceptors for photoexcited electrons of CPs. According to this mechanism, introducing electron-rich units into the CPs is another important strategy besides introducing bulky rigid blocks, which facilitates the electron-transfer from CPs to NACs.

Poly(phenylene ethynylene)s (PPEs) based CPs for detecting NACs have been extensively investigated due to that the rigid three-dimensional pentiptycenes can be facily introduced to the backbone of PPEs to prevent  $\pi$ – $\pi$  stacking between backbones [21–28]. However, reports about poly(fluorenylene ethynylene)s (PFEs), which are analogues of PPEs, are extremely rare in this field, although PFEs exhibit many potential abilities to act as NACs sensors, such as good electron conductivity, strong fluorescence intensity and facile substitution on  $C_9$  position [29,30]. Nevertheless, new structural modification is required to improve the permeability and electron-transfer ability of PFEs, so as to enhance their sensing sensitivity to NACs.

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In this work, four PFEs-based CPs have been synthesized by introducing 9,9-diphenylfluorene units and/or thiophene units into the backbone of PFEs (Fig. 1). 9,9-Diphenylfluorene is expected to weaken the  $\pi$ - $\pi$  stacking between backbones and improve the permeability of the polymer due to its rigid steric hindrance, while electron-rich thiophene can promote electron-transfer from CPs to NACs. The effect of different polymer structure on the sensing performance will be discussed in details in the third part of this article

## 2. Experimental

### 2.1. Materials and measurements

All the organic reagents and solvents used in this work were purchased from Aladdin Industrial Corporation, except that 2,5-diyne-9,9-dihexyl-fluorene was synthesized according to the reported methods [31]. THF was distilled over sodium in the presence of benzophenone under  $N_2$  atmosphere before use. The diisopropylamine, toluene and triethylamine were dried by  $CaH_2$ . The analytes for fluorescence quenching studies, such as 2,4-dinitrotoluene (DNT), picric acid (PA) and *p*-benzoquinone (BQ), were obtained from Aldrich. A small amount of 2,4,6-trinitrotoluene (TNT) was prepared in our laboratory.

The  $^1H$  NMR spectra were recorded on AVANZC II 400 spectrometers using  $CDCl_3$  or  $DMSO-d_6$  as solvent. The elemental analyses were characterized by a Flash EA1112, CHNS-O elemental analysis

instrument. DSC spectra were performed on a NETSCH (DSC-204) unit at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under nitrogen. Thermal gravimetric analysis (TGA) was performed with a Pyris1 TGA thermal analysis system at heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  under nitrogen. UV-vis absorption spectra were recorded on a UV-2500 spectrophotometer. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using THF as the eluent and polystyrene as standard. The AFM images were recorded on Multimode 8 Nanoscope V system with the scanning area  $2 \times 2\text{ }\mu\text{m}$  or  $1 \times 1\text{ }\mu\text{m}$ .

The fluorescence spectra were measured with F-4600 fluorescence spectrophotometer. The quenching efficiency of polymers in DNT/THF solution was measured according to the following procedures: To each of twenty volumetric flasks (5 ml), 50  $\mu\text{L}$  solution of polymers in THF ( $C = 10^{-3}\text{ g/L}$ ) was added. Then 0–2000  $\mu\text{L}$  solutions of DNT in THF ( $C = 10^{-1}\text{ g/L}$ ) was added to the flasks. Subsequent dilution with THF gave a series of  $10^{-5}\text{ g/L}$  polymer solutions with the concentration of DNT varying from 0 to  $2.1 \times 10^{-4}\text{ mol/L}$ . The emission data of these solutions were collected with an excitation wavelength of 371 nm, 380 nm, 365 nm and 390 nm for  $P_1$ ,  $P_2$ ,  $P_3$  and  $P_4$  respectively.

The quenching efficiency of polymer films in saturated DNT vapor was measured according to the following procedures: to a cuvette with a lid, 100 mg DNT was added with a piece of filter paper covering on the DNT solid to prevent direct contact between the DNT and the film. Then the cuvette was laid aside for 3 h at room temperature to allow the solid–vapor equilibrium established. After

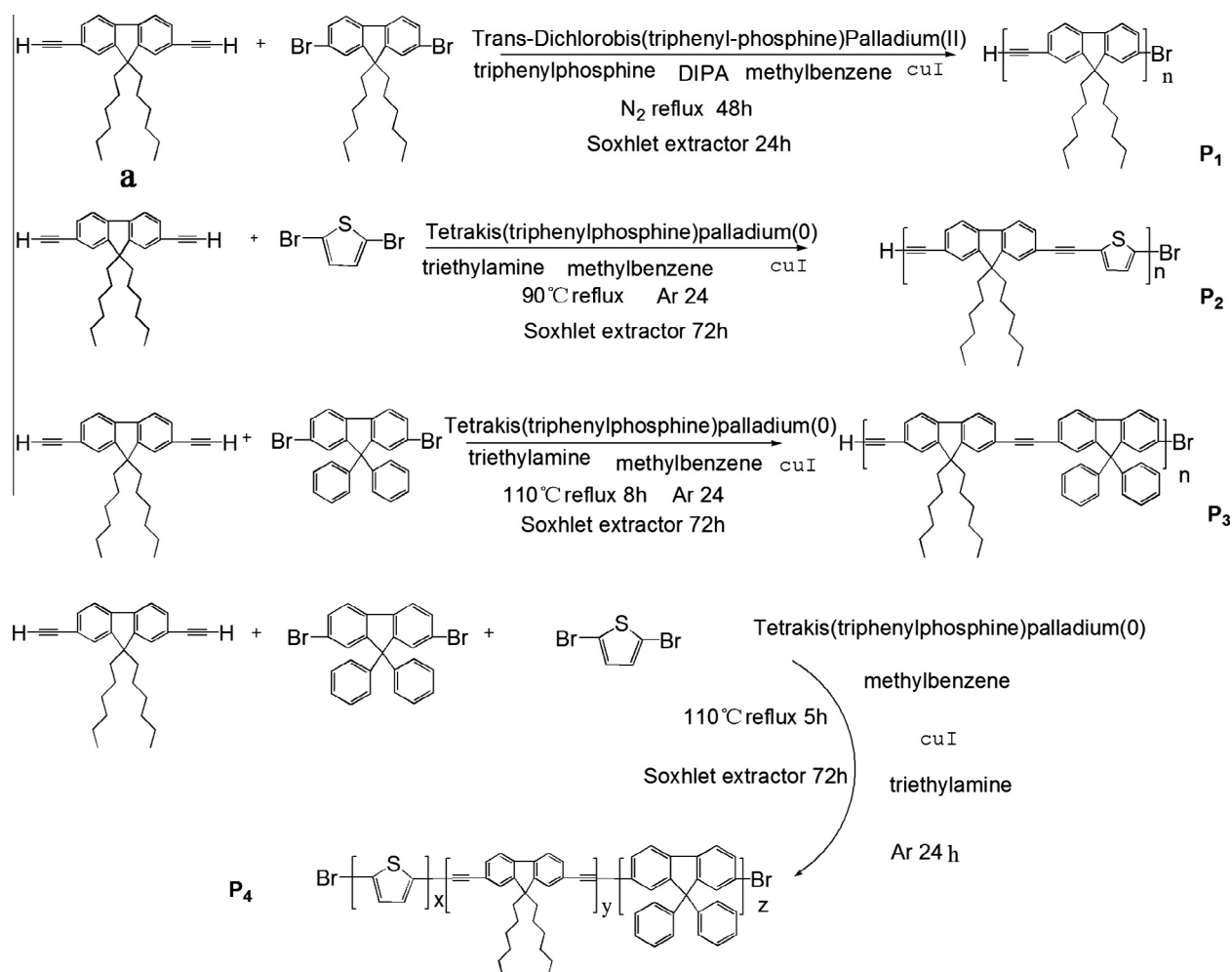


Fig. 1. Syntheses of conjugated polymers  $P_1$ ,  $P_2$ ,  $P_3$  and  $P_4$ .

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