



# Synthesis of a novel fluorene-based conjugated polymer with pendent bulky caged adamantane moieties and its application in the detection of trace DNT explosives

HongFei Leng, WenHui Wu\*

School of Material Science and Engineering, Beijing Institute of Technology, Beijing 100081, China

## ARTICLE INFO

### Article history:

Received 23 September 2011

Received in revised form 7 January 2012

Accepted 9 January 2012

Available online 18 January 2012

### Keywords:

Conjugated polymers  
Fluorescence quenching  
Adamantane moieties  
High sensitivity  
Explosives detection

## ABSTRACT

A novel fluorene-based conjugated polymer with phenylene spacers and steric bulky adamantane moieties in side chains has been synthesized by palladium-catalyzed Suzuki coupling reactions. This design strategy offers several advantages for the detection of trace 2,4-dinitrotoluene (DNT) vapor. The incorporation of the two groups into polymer side chains could retain an effective conjugation length and prevent the  $\pi$ -stacking of polymer chains. The detection of DNT vapor indicated that the polymer displayed higher fluorescence quenching sensitivity toward the explosives in films compared to reference polymers. The fluorescence quenching efficiency of the fluorescent polymer achieved 33.3% in 10 s and 71.1% in 60 s. The pathways or cavities generated by the two spacers are beneficial for the rapid diffusion of explosive vapor into the film interiors and increase the fluorescence quenching efficiency of the film.

© 2012 Elsevier Ltd. All rights reserved.

## 1. Introduction

The rise in security issues and threats across the globe has required that methods for trace explosives detection are sensitive, inexpensive and selective. The most common methods for the detection of explosives, such as gas chromatography, ion mobility spectrometry, X-ray imaging and electrochemistry, have some disadvantages. For example, the instruments previously mentioned are expensive, and their operating procedures are complicated. In contrast, the design and fabrication of chemical sensors has attracted considerable interest because of their easy operation, low cost and rapid detection capabilities [1–5]. Furthermore, conjugated polymers based on fluorescence quenching are proven to be one of the most sensitive and convenient methods for the detection of nitroaromatic-based explosives [6–8]. Hence a series of conjugated polymers, such as polysilanes, poly(*p*-phenyleneethynylenes), polymetalloles, polyacetylene and poly(*p*-phenylenevinylene), etc. were prepared as sensing materials for trace explosives detection [9–14].

However,  $\pi$ -stacking of the conjugated polymers in the solid-state (thin film) form leads to significant fluorescence self-quenching and is a major disadvantage encountered in the application of chemical sensors [15–17]. Several methods have been developed to prevent the  $\pi$ - $\pi$  stacking of the conjugated chains. Designing star-like, hyper-branched and cross-linked architectures, copolymerizing with bulky spacers and chemically grafting

with non-conjugated side groups are effective methods to prevent chain aggregation [18–22]. Among these methods, introducing bulky spacers into polymer backbones or side chains is an effective approach. For example, adamantane is a bulky hydrocarbon, consisting of four cyclohexanes fused into a chair conformation. Li et al. synthesized poly(fluorene-co-adamantane) as a blue light emitting polymer [23]. However, the average molecular weight ( $M_n$ ) of the copolymer was only 2700. We modified the adamantane units and synthesized 1,3-bis(4-bromo-benzylideneamino)adamantane with higher reactivity. We also prepared a series of polyfluorenes with adamantane derivatives as inserted-backbone units with higher molecular weights (the  $M_n$  was approximately  $2.0 \times 10^4$ ) [24]. However, non-conjugated adamantane groups inserted into the polymer backbone can lead to a shorter effective conjugation length [25,26], and this could lower the sensitivity of the polymer when used for sensing applications.

Herein, we report the synthesis of a novel polymer that displays a valid isolation effect on the main chain, where the main chain contains phenylene spacers in the C-9 carbon of fluorene units and adamantane moieties in side chains. For the designed polymer, the incorporation of adamantane units into the side chains was expected to maintain the effective conjugation length of the conjugated polymer and the amplified signal of fluorescence quenching toward explosives. To demonstrate the chain-isolated effect and the high response to DNT of the bulky adamantane groups as well as the presence of the rigid phenylene spacer introduced in the side chains, two reference polymers with the same backbone have also been synthesized. The fluorescence properties of the conjugated polymers and their sensing performances toward DNT vapor are

\* Corresponding author. Tel.: +86 10 68912659.

E-mail address: [wuw@bit.edu.cn](mailto:wuw@bit.edu.cn) (W.H. Wu).

investigated. To the best of our knowledge, such polymers have not been reported in the literature to date and are expected to improve the sensing capabilities for explosives.

## 2. Experimental procedure

### 2.1. Materials

1-Adamantanol was purchased from OrgSynChem Technology Co., Ltd. 2,7-dibromo-9-fluorenone and phenol were supplied by Aladdin-Reagent Co., Ltd. 9,9-dihexyl-2,7-dibromofluorene, benzen-1,4-bis(boronic acid)propane-1,3-diol and tetrakis(triphenylphosphine) palladium were obtained from Synwit Technology Co., Ltd. Other reagents and solvents obtained from commercial suppliers were used without further purification.

### 2.2. Instrumentation

All new compounds were identified by  $^1\text{H}$  NMR and FT-IR.  $^1\text{H}$  spectra were recorded on a Bruker AVANCE DRX 400 NMR spectrometer. FT-IR spectra were obtained using a Bruker TENSOR 27 with samples prepared as KBr disk pellets. Gel permeation chromatography (GPC) was carried out on a Waters GPC515-2410 System with THF as an eluent. UV-Vis absorption and photoluminescence (PL) spectra of polymers were recorded using a Shimadzu UV-1700 Ultraviolet Spectrophotometer and a Hitachi F-4500 Fluorescence Spectrophotometer, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  using a TA TG2050 and a DSC910S, respectively.

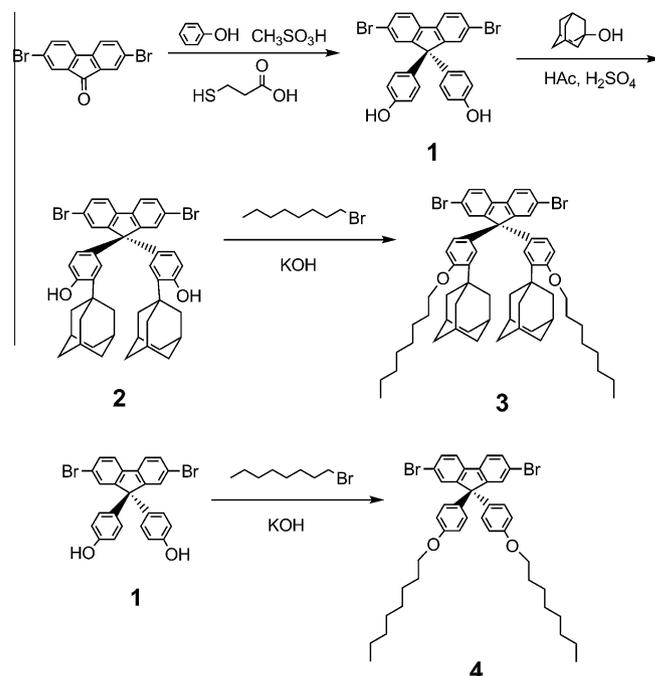
### 2.3. Synthesis of monomers

#### 2.3.1. (2,7-Dibromo-9,9-bis(4-hydroxyphenyl))fluorene(1)

A three-neck 100 mL flask was filled with phenol (13.160 g, 140 mmol) and 2,7-dibromofluorene-9-one (4.732 g, 14 mmol). Methanesulfonic (20 mL) and mercaptopropionic (0.075 g, 0.708 mmol) were added to the mixture and then reacted for 16 h at  $50\text{ }^\circ\text{C}$ . The reaction mixture was then poured into 500 mL of cold water. The residue was washed with hot water several times. Petroleum ether was added to the crude products dissolved in ethyl acetate, and then the precipitate was collected and dried in a vacuum oven to provide a light brown solid, monomer **1** (6.11 g, 86%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 M Hz, ppm):  $\delta$  9.41 (s, 2 H, -OH), 7.89 (d, 2H, Ar-H), 7.55 (d, 2 H, Ar-H), 7.47 (s, 2 H, Ar-H), 6.87 (d, 4 H, Ar-H), 6.65 (d, 4 H, Ar-H). FT-IR (film,  $\text{cm}^{-1}$ ):  $\nu$  3296 (Ar-OH), 3060 (Ar H), 1175, 1053 (C-Br).

#### 2.3.2. Bisubstituted (2, 7-dibromo-9,9-bis(4-hydroxyphenyl))fluorene with adamantane moieties (2)

1-Adamantanol (2.736 g, 18 mmol) and monomer **1** (4.572 g, 9 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (30 mL) at  $0\text{ }^\circ\text{C}$ , and then a mixture of 98%  $\text{H}_2\text{SO}_4$  (1.5 mL) and AcOH (7.5 mL) was added slowly dropwise over 20 min. After 21 h of stirring at room temperature, the resulting mixture was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ , and the organic phase was dried over sodium sulfate. After the removal of solvent at reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v 1/6) as an eluent. White solid **2** was obtained by evaporating of the eluent (4.54 g, 65%). In this reaction, **2** may have three ortho-isomers, so **2** in Scheme 1 was representative of one of the three isomer structures.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 M Hz,



Scheme 1. Synthetic routes to monomers (3 and 4).

ppm):  $\delta$  7.57 (d, 2 H, Ar-H), 7.45 (d, 2 H, Ar-H), 7.39 (d, 2 H, Ar-H), 7.19 (d, 2 H, Ar-H), 6.58 (s, 2 H, Ar-H), 6.45 (d, 2 H, Ar-H), 4.76 (s, 2 H, -OH), 2.05 (m, 18 H, Ad-H), 1.75 (s, 12 H, Ad-H). FT-IR (film,  $\text{cm}^{-1}$ ):  $\nu$  3550 (Ar-OH), 3035 (Ar H), 2905, 1358, 1305, (Ad H), 1118, 1061 (C-Br).

#### 2.3.3. Adamantane substituted (2, 7-dibromo-9,9-bis(4-octyloxyphenyl))fluorene (3)

**2** (1.552 g, 2 mmol) and KOH (0.448 g, 8 mmol) were mixed in 25 mL of ethanol. The reaction mixture was heated to  $80\text{ }^\circ\text{C}$  for 0.5 h, and then bromooctane (1.2 g, 6 mmol) was added slowly dropwise into the reaction mixture. The solution was kept at  $80\text{ }^\circ\text{C}$  for 20 h. After the reaction was complete, the mixture was poured into water (300 mL), extracted with ethyl acetate and dried over  $\text{MgSO}_4$ . After removal of the organic solvent, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v 1/15) as an eluent to yield white solid **3** (1.70 g, 85%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 M Hz, ppm):  $\delta$  7.56 (d, 2 H, Ar-H), 7.45 (d, 2 H, Ar-H), 7.39 (d, 2 H, Ar-H), 7.25 (d, 2 H, Ar-H), 6.85 (s, 2 H, Ar-H), 6.62 (d, 2 H, Ar-H), 3.90 (s, 4 H,  $\text{OCH}_2$ ), 2.03 (m, 18 H, Ad-H), 1.83 (m, 12 H, Ad-H), 1.74 (m, 4 H,  $\text{CH}_2$ ), 1.52 (m, 4 H,  $\text{CH}_2$ ), 1.32 (m, 16 H,  $\text{CH}_2$ ), 0.87 (m, 6 H,  $\text{CH}_3$ ).

#### 2.3.4. (2,7-Dibromo-9,9-bis(4-octyloxyphenyl))fluorene (4)

Monomer **1** (1.016 g, 2 mmol) and KOH (0.448 g, 8 mmol) were mixed in 25 mL of ethanol. The reaction mixture was heated to  $80\text{ }^\circ\text{C}$  for 0.5 h, then bromooctane (1.2 g, 6 mmol) was added slowly dropwise into the reaction mixture. The solution was kept at  $80\text{ }^\circ\text{C}$  for 20 h. After the reaction was complete, the mixture was poured into water (300 mL), and extracted with ethyl acetate. After removal of the organic solvent at reduced pressure, the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v 1/6) as an eluent to yield white solid **4** (1.30, 89%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 M Hz, ppm):  $\delta$  7.56 (d, 2 H, Ar-H), 7.47 (d, 2 H, Ar-H), 7.44 (d, 4 H, Ar-H), 7.04 (d, 2 H, Ar-H), 6.71 (s, 4 H, Ar-H), 3.89 (s, 4 H,  $\text{OCH}_2$ ), 1.76 (m, 4 H,  $\text{CH}_2$ ), 1.44 (m, 4 H,  $\text{CH}_2$ ), 1.29 (m, 16 H,  $\text{CH}_2$ ), 0.87 (m, 6 H,  $\text{CH}_3$ ).

#### 2.4. General procedure for synthesis of polymers PF1–PF3

General synthetic procedures for the polymers PF1–PF3 can be described as follows. To a solution of fluorene derivatives (monomers 3–5) and benzen-1,4-bis(boronic acid)propane-1,3-diol in THF, aqueous potassium carbonate (2 M) was added. The mixture was stirred and degassed with nitrogen for 15 min, and a catalytic amount of tetrakis(triphenylphosphine) palladium ( $\text{Pd}(\text{PPh}_3)_4$ ) (2.0 mol%) was added quickly. The solution was then stirred at 69 °C for 48 h, and the mixture was cooled and poured into methanol. The precipitates were collected by filtration and washed copiously with methanol and water several times. After the organic solvents and water were removed, the solid was washed with acetone to remove oligomers and catalyst residues. Finally, the product was obtained after being dried at 40 °C under vacuum for 1 day.

**PF1: 3** (1.000 g, 1 mmol), benzen-1,4-bis(boronic acid)propane-1,3-diol (0.246 g, 1 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.024 g, 0.018 mmol) and 2 M aqueous  $\text{Na}_2\text{CO}_3$  solution (10 mL) were used for the synthesis of PF1. The obtained solid was a light yellow powder (0.632 g, 69%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.83 (d, 2 H, Ar-H), 7.50–7.61 (m, 6 H, Ar-H), 7.31–7.46 (m, 4 H, Ar-H), 6.85 (d, 2 H, Ar-H), 6.64 (d, 2 H, Ar-H), 3.90 (s, 4 H,  $\text{OCH}_2$ ), 2.07 (m, 18 H, Ad-H), 1.87 (m, 12 H, Ad-H), 1.75 (m, 4 H,  $\text{CH}_2$ ), 1.53 (s, 4 H,  $\text{CH}_2$ ), 1.41–1.22 (m, 16 H,  $\text{CH}_2$ ), 0.87 (m, 6 H,  $\text{CH}_3$ ).

**PF2: 4** (0.732 g, 1 mmol), benzen-1,4-bis(boronic acid)propane-1,3-diol (0.246 g, 1 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.024 g, 0.018 mmol) and 2 M aqueous  $\text{Na}_2\text{CO}_3$  solution (10 mL) were used for the synthesis of PF2. The obtained solid was a yellow powder (0.505 g, 78%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.86 (d, 2 H, Ar-H), 7.39–7.68 (m, 8 H, Ar-H), 7.26 (d, 4 H, Ar-H), 6.82 (d, 4 H, Ar-H), 3.93 (s, 4 H,  $\text{OCH}_2$ ), 1.78 (m, 4 H,  $\text{CH}_2$ ), 1.46 (m, 4 H,  $\text{CH}_2$ ), 1.31–1.20 (m, 16 H,  $\text{CH}_2$ ), 0.91 (m, 6 H,  $\text{CH}_3$ ).

**PF3: 5** (0.492 g, 1 mmol), benzen-1,4-bis(boronic acid)propane-1,3-diol (0.246 g, 1 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.024 g, 0.018 mmol) and 2 M aqueous  $\text{Na}_2\text{CO}_3$  solution (10 mL) were used for the synthesis of PF3. The obtained solid was a light gray powder (0.330 g, 81%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm):  $\delta$  7.83 (d, 4 H, Ar-H), 7.67 (d, 2 H, Ar-H), 7.31 (d, 4 H, Ar-H), 2.11 (m, 4 H,  $\text{CH}_2$ ), 1.27–1.11 (m, 16 H,  $\text{CH}_2$ ), 0.81 (m, 6 H,  $\text{CH}_3$ ).

#### 2.5. Fabrication of sensing films

The films PF1–PF3 were prepared by a conventional spin-casting technique. In brief, the polymer solution (0.5 mg in 1.0 mL THF) was spin-coated onto a glass plate (microscope slide, length: 24 mm, width: 24 mm and thickness: 1 mm) at a spin rate of 1000 rpm. Then, the films were dried at 30 °C under vacuum for 1 day to remove any residue in the films.

### 3. Results and discussion

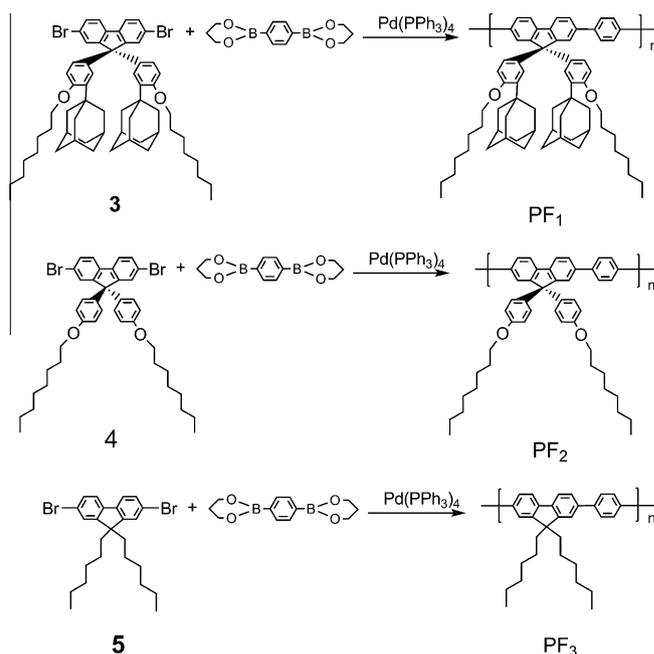
#### 3.1. Synthesis and characterization

Our strategy for the synthesis of the monomers is outlined in Scheme 1, where 7-dibromofluorene-9-one in phenol and methanesulfonic acid in the presence of a catalytic amount of mercaptopropionic acid afforded compound 1. The acid-catalyzed Friedel–Crafts reaction of 1 and 1-Adamantanol gave bisubstituted 2 which was confirmed by  $^1\text{H}$  NMR (see Supplementary Fig S1). The eighteen hydrogen atoms at 2.05 ppm and the twelve hydrogen atoms at 1.75 ppm indicated that two adamantane units were incorporated into monomer 1. As described in the literature [27], the hydrogen atom at ortho-position of the phenolic hydroxyl group is substituted with adamantane units by Friedel–Crafts alkylation. In this reaction, ortho-isomers of monomer 2 may exist, and these

isomers were used for the next synthesis without separation. Monomers 3 and 4 were synthesized from the reaction of 2 and 3 with bromooctane in the presence of KOH. As shown in Scheme 2, PF1–PF3 were prepared by a palladium-catalyzed Suzuki cross-coupling reaction.

The obtained polymers are completely soluble in common organic solvents, such as THF, DMF, toluene, and chloroform. The GPC analysis indicated that the number-average molecular weight of PF1 was 7900 with a 2.73 polydispersity index (PDI), that of PF2 was 6400 with a 2.11 polydispersity index (PDI) and that of PF3 was 7800 with a 2.15 polydispersity index (PDI).

The thermal stability of polymers PF1–PF3 were characterized by thermogravimetric analysis (TGA). As shown in Fig. 1, the thermal decomposition temperatures ( $T_d$ , 95 wt.% residue) of PF1–PF3 were 387 °C, 381 °C and 416 °C in nitrogen, respectively. This demonstrated that the three polymers were thermally stable enough for use as sensing films at ambient temperatures. The glass transition temperatures ( $T_g$ ) of polymers PF1–PF3 were characterized by differential scanning calorimetry (DSC) (see Supplementary Fig S4). The  $T_g$  of PF1 was not observed up to 152 °C, which was higher than for the other two polymers. This suggests that the chain



Scheme 2. Synthetic routes to polymers (PF1–PF3).

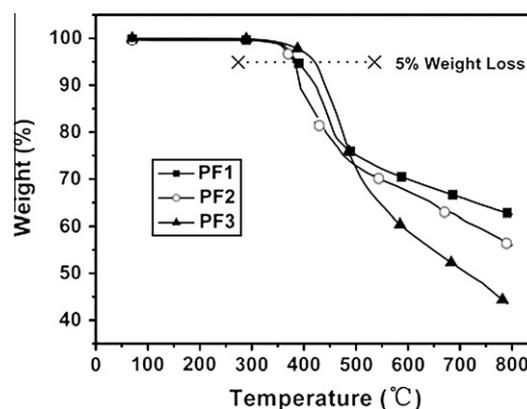


Fig. 1. TG curves of polymers PF1–PF3.

mobility of this polymer was effectively suppressed by the incorporation of the rigid adamantane component. In addition, the absorption and fluorescence spectra of the three polymers were not changed in solution (such as THF,  $\text{CHCl}_3$ , DMF and toluene) for 1 month, thereby indicating that they were stable in solvents.

### 3.2. Photophysical properties

The photophysical properties of PF1–PF3 were examined in both THF solution and the solid films. The absorption and PL spectra in films are shown in Fig. 2. The absorption and fluorescence spectra of the three polymers in THF solution are similar (see Supplementary Fig S3). This is because the conjugated polymers can disperse well in the THF solution, and chain aggregation among the three polymers was either very weak or did not exist.

The absorption peaks for PF1–PF3 in the solid state were shifted by approximately 5 nm, 21 nm and 24 nm to longer wavelengths compared with that in THF, respectively. In addition, the obvious green emission peak at 520 nm for PF2 and PF3 as a film were much stronger than that of PF1, and this correlated to aggregation of polymer chains in the solid state [18,19]. The red shift in the absorption spectra of PF2 was shorter than that of PF3, and the green emission peak of PF2 at 520 nm was also weaker than that of PF3. This revealed the phenylene spacer can prevent interchain interactions in the solid state, and the bulky adamantane moieties could further effectively suppress the aggregation of polymer chains in the film.

The fluorescence quantum efficiency of PF1–PF3 in THF solution was similar ( $\Phi_{\text{PL}}$  was estimated using quinine sulfate in 0.05 M  $\text{H}_2\text{SO}_4$ ,  $\Phi_{\text{PL}} = 0.546$ ). However, as we expected, the  $\Phi_{\text{PL}}$  of the three polymers is ordered as follows: PF1 (0.58) > PF2 (0.45) > PF3 (0.42) in the film state. The higher  $\Phi_{\text{PL}}$  of PF2 versus PF3 was attributed to the phenylene units in the C-9 carbon of fluorene groups, as these have steric hindrance effects on the main chains of the polymers [28]. The improvement  $\Phi_{\text{PL}}$  of PF1 can be attributed to the adamantane moieties, thereby sterically isolating the polymer backbones and reducing self-quenching that usually accompanies the solid state form. The adamantane moieties have both positive and negative effects on the  $\Phi_{\text{PL}}$  of PF1, as it is a non-conjugated group. However, the higher  $\Phi_{\text{PL}}$  of PF1 indicated that the positive effect was the leading factor, so the  $\Phi_{\text{PL}}$  of PF1 was increased. Both the phenylene and adamantane moieties in the side chains benefit the higher  $\Phi_{\text{PL}}$  of PF1 in the film state.

### 3.3. Fluorescence quenching characteristics of PF1–PF3 to DNT in solution

The fluorescence quenching of PF1–PF3 to DNT as a representative nitroaromatic-based explosive was studied in THF. The

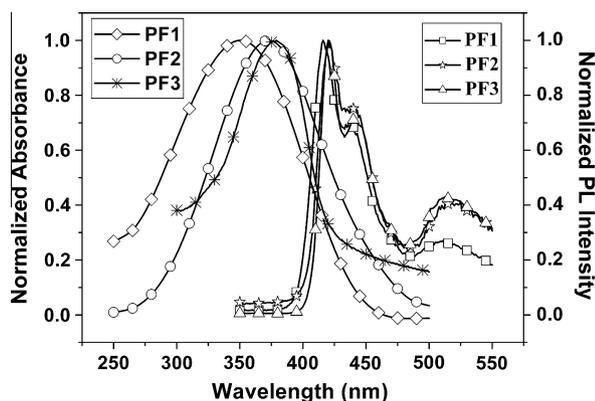


Fig. 2. Absorption and PL spectra of PF1–PF3 in films.

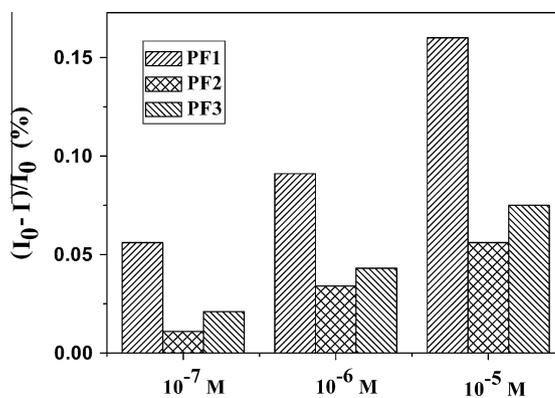


Fig. 3. The fluorescence quenching efficiencies of PF1–PF3 in THF solution toward DNT.

fluorescence quenching efficiencies (FQEs) of PF1–PF3 in THF are shown in Fig. 3. The fluorescence quenching efficiency (FQE) is defined as  $(I_0 - I)/I_0 \times 100\%$ , where  $I_0$  and  $I$  are the fluorescence intensity in the absence and presence of DNT, respectively. Compared with PF2 and PF3, PF1 exhibited a higher FQE to DNT. The sensitivity of PF1 to DNT in THF may be related to the more structurally restricted environment of PF1, as PF1 may cause the DNT to be effectively “bound” to the polymer backbones rather than simply diffuse through, and this can effectively increase the probability of charge-transfer [29]. As indicated in early literature [30], the fluorescence quenching of polymers is affected by the binding strength between polymers and analytes, so the higher FQE of PF1 may be related to the higher binding strength between PF1 and DNT molecules.

### 3.4. Fluorescence quenching characteristics of PF1–PF3 to DNT vapor in films

Fluorescence response experiments for the three polymers to the DNT vapor were performed in the following manner [30]. Briefly, the film was inserted into a glass bottle containing a small amount of DNT powder and cotton gauze (to help maintain a constant saturated vapor pressure at room temperature and prevent the film from directly contacting the DNT powder). By measuring the fluorescence intensity of the film after exposure to the DNT vapor for different time periods, a time-dependence of the fluorescence quenching was obtained.

Fig. 4 shows the time-dependent fluorescence intensities for PF1 films upon exposure to DNT vapor. The fluorescence intensity of PF1 gradually decreased over time after exposure to the DNT vapor. The FQE at different time periods of exposure to the DNT vapor is shown in Fig. 5. Rapid PL quenching was observed for PF1 upon exposure to the DNT vapor. For example, the FQE of PF1 was 33.3% in 10 s. However, the FQE of PF2 and PF3 were only 8.2% and 6.1% in 10 s, respectively. Compared with PF2 and PF3, PF1 was four-fold more sensitive toward the DNT vapor. After exposure to the DNT vapor for 300 s, the FQE of PF1 was 91.6%, and this was similar to that of poly(iptycenebutadiynylene) derivatives reported by Swager's group (which was 90% around in 300 s) [29]. As we expected, the PF1 film showed higher sensitivity than the other two polymers after exposure to DNT vapor.

Clearly, the presence of the phenylene and adamantane moieties in PF1, which maintain a high fluorescence quantum efficiency, is a reasonable explanation for the observed enhanced fluorescence quenching efficiency. Furthermore, the incorporation of bulky three-dimensional adamantane groups and phenylene spacers introduce pathways or cavities in the solid-state material. These

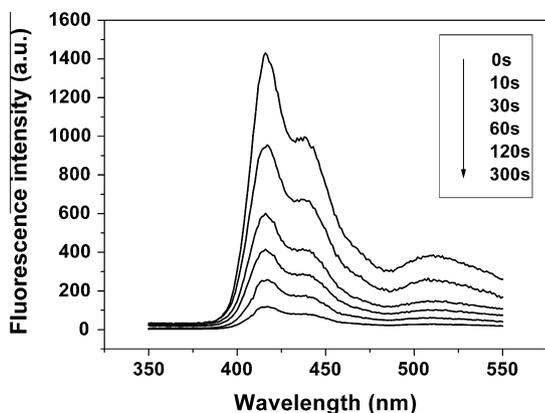


Fig. 4. Time-dependent fluorescence intensities of PF1 upon exposure to DNT vapor in different time intervals.

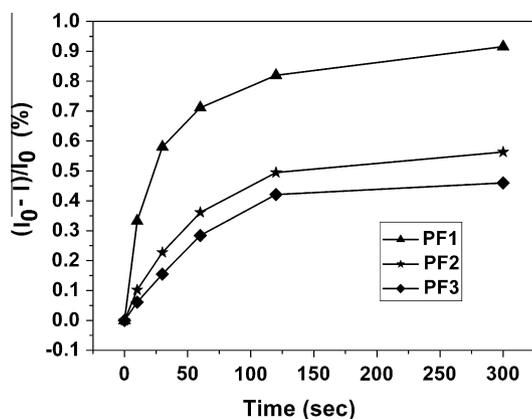


Fig. 5. Time-dependence of FQE of synthesized polymers in thin films upon exposure to DNT vapor at different times.

were suitable for accommodating DNT molecules and made the diffusion of the DNT molecules into the films easier. These also enhanced charge-transfer from the excited polymer backbone to the DNT molecules and have a rapid response. Although the polymers with adamantane moieties inserted into the backbone can generate a larger free volume in the solid state, as suggested in the literature of Li [23], the adamantane units in the backbone interrupt the conjugated structure of the polymer and separate

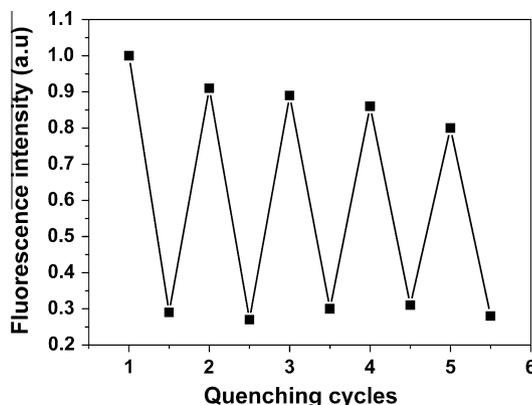


Fig. 6. The fluorescence quenching-recovery cycles test for the PF1 film. The quenching time was 60 s. After each quenching cycle, the PF1 film was recovered by immersing it in methanol for 20 min.

the backbones into several isolated shorter conjugated chain segments. Therefore, the conjugated polymers' superiority of amplified fluorescence quenching will disappear [30]. So, the introduction of adamantane moieties into side chains can maintain the long conjugated length of the polymer chain and the high sensitivity towards explosives.

The fluorescence quenching-recovery of the PF1 thin film has also been tested. Fig. 6 shows the results of fluorescence quenching-recovery cycles. After exposure to DNT explosive vapor, the film's fluorescence intensity can be slowly recovered by exposure to air for a few days or quickly recovered by immersing in methanol for 20 min followed by drying in air. The recovered film showed similar quenching efficiency when re-exposed to the vapor of the DNT explosive. This indicates that the film could be used repeatedly. Efficient quenching and recovery were obtained for repeated use, and this implies a good reversibility of the material and a high fluorescence stability for the film against photobleaching.

#### 4. Conclusion

In this work, we have synthesized a novel fluorescent polymer containing phenylene and adamantane moieties as side groups through a typical Pd catalyzed Suzuki coupling reaction. The incorporation of adamantane units into the side chain (versus insertion into the backbone) maintains the effective conjugation length of conjugated polymer and the higher FQE towards DNT. It is shown that the incorporation of the rigid three-dimensional structure of adamantane moieties and phenylene spacers could effectively suppress interchain interactions and generate pathways or cavities that can improve the diffusion of explosive molecules into films, and thus increase the fluorescence quenching efficiency toward DNT in films.

#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.reactfunctpolym.2012.01.002](https://doi.org/10.1016/j.reactfunctpolym.2012.01.002).

#### References

- [1] S. Malashikhin, N.S. Finney, *Journal of the American Chemical Society* 130 (2008) 12846–12847.
- [2] G. He, G. Zhang, F. Lu, Y. Fang, *Chemistry of Materials* 21 (2009) 1494–1499.
- [3] S. Tao, Y. Li, G. Li, C. Yu, *Journal of Materials Chemistry* 18 (2008) 4426–4432.
- [4] D.A. Oriero, J.M.F. Jabal, L. Deobald, A.T. Weakley, D.E. Aston, *Reactive and Functional Polymers* 71 (2011) 870–880.
- [5] T. Saitoh, Y. Sugiura, K. Asano, M. Hiraide, *Reactive and Functional Polymers* 69 (2009) 792–796.
- [6] T.M. Swager, *Accounts of Chemical Research* 31 (1998) 201–207.
- [7] Q. Chen, Y. Cui, T.L. Zhang, J. Cao, B.H. Han, *Biomacromolecules* 11 (2010) 13–19.
- [8] H. Li, J. Wang, Z. Pan, L. Cui, L. Xu, R. Wang, Y. Song, L. Jiang, *Journal of Materials Chemistry* 21 (2011) 1730–1735.
- [9] A.E. Rose, Z. Zhu, C.F. Madigan, T.M. Swager, V. Bulović, *Nature* 434 (2005) 876–879.
- [10] J. Yang, S. Aschemeyer, H.P. Martinez, W.C. Trogler, *Chemical Communications* 46 (2010) 6804–6806.
- [11] Z. Wang, Z.Y. Wang, J. Ma, W.J. Bock, D. Ma, *Polymer* 51 (2010) 842–847.
- [12] C. Zhang, Y. Che, X. Yang, B.R. Bunes, L. Zang, *Chemical Communications* 46 (2010) 5560–5562.
- [13] H. Nie, Y. Zhao, M. Zhang, Y. Ma, M. Baumgarten, K. Müllen, *Chemical Communications* 47 (2011) 1234–1236.
- [14] K.A. Vishnumurthy, M.S. Sunitha, R. Philip, A.V. Adhikari, *Reactive and Functional Polymers* 71 (2011) 1119–1128.
- [15] C.W. Wu, C.M. Tsai, H.C. Lin, *Macromolecules* 39 (2006) 4298–4305.
- [16] S. Chen, Q. Zhang, Q. Liu, J. Gu, L. Zhang, J. Zhou, X. Fan, L. Fang, *Reactive and Functional Polymers* 71 (2011) 1008–1015.
- [17] R. Scaria, N.T. Lucas, K. Müllen, J. Jacob, *Reactive and Functional Polymers* 71 (2011) 849–856.
- [18] J.P. Du, Q. Fang, D.S. Bu, S.J. Ren, A. Cao, X.Y. Chen, *Macromolecular Rapid Communications* 26 (2005) 1651–1656.
- [19] W.J. Lin, W.C. Chen, W.C. Wu, Y.H. Niu, A.K.Y. Jen, *Macromolecules* 37 (2004) 2335–2341.

- [20] Q.J. Zhao, W.H. Wu, *Polymer* 50 (2009) 998–1004.
- [21] T. Morikita, T. Yasuda, T. Yamamoto, *Reactive and Functional Polymers* 68 (2008) 1483–1491.
- [22] I. Yamaguchi, H. Mitsuno, *Reactive and Functional Polymers* 71 (2011) 140–147.
- [23] J. Li, Y. Hirayama, T. Sano, T. Tomita, H. Fujii, K. Wakisaka, *Thin Solid Films* 515 (2006) 2686–2691.
- [24] Q.J. Zhao, W.H. Wu, *Synthetic Metals* 159 (2009) 1153–1157.
- [25] S.Y. Zheng, J.M. Shi, R. Mateu, *Chemistry of Materials* 12 (2000) 1814–1817.
- [26] J.A. Mikroyannidis, K.Y. Cheung, M.K. Fung, A.B. Djurišić, *Reactive and Functional Polymers* 70 (2010) 426–432.
- [27] Z. Liu, J. Xiang, *Organic Process Research & Development* 10 (2006) 285–288.
- [28] C.-R. Yin, S.-H. Ye, J. Zhao, M.-D. Yi, L.-H. Xie, Z.-Q. Lin, Y.-Z. Chang, F. Liu, H. Xu, N.-E. Shi, Y. Qian, W. Huang, *Macromolecules* 44 (2011) 4589–4595.
- [29] D. Zhao, T.M. Swager, *Macromolecules* 38 (2005) 9377–9384.
- [30] J.-S. Yang, T.M. Swager, *Journal of the American Chemical Society* 120 (1998) 11864–11873.