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Crosslinked fluorescent conjugated polymer nanoparticles for high performance explosive

sensing in aqueous media

Wenyue Dong^a, Zhihua Ma^a, Qian Duan^{a,*}, Teng Fei^{b,*}

^a School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, P.R. China

^b State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, P.R. China

*Corresponding author:

duanqian@cust.edu.cn (Q. Duan)

feiteng@jlu.edu.cn (T. Fei)

Abstract

In this work, water dispersible crosslinked fluorescent poly(triphenylamine-*co*-benzothiadiazole)s (PTPABT) nanoparticles have been synthesized *via* Suzuki-type coupling $(A_3 + B_2)$ in a toluene/water miniemulsion. Dialysis method was used to purify the PTPABT nanoparticles with a diameter range of 40-70 nm. The good dispersion property of the polymer in water could be attributed to the small sizes of the PTPABT nanoparticles. The obtained PTPABT nanoparticles possess microporous characteristic and display bright red emission in aqueous solution, which makes them possible to detect the nitro-aromatic explosive in aqueous media by monitoring the photoluminescence. The sensing property of the polymer nanoparticles towards 1,3,5-trinitrobenzene (TNB) in aqueous media has been researched, resulting a Stern-Volmer quenching constant K_{sv} of 1.22×10^4 M⁻¹. The most attractive character of the conjugated polymer nanoparticles is the combination of both physical stability and solution-processability, thus making them good candidates for sensors and optoelectronic applications.

Keywords Polymerization in miniemulsion; Crosslinked fluorescent polymer; Porous nanoparticles; Explosive detection

1. Introduction

The detection of nitro-aromatic explosives is of great importance for global security and environmental protection in the past few decades [1,2]. It is well known that nitro-aromatic explosives are not only dangerous component in landmines but also identified as pollutants in soil or water, which may cause harmful damage to human nerves and visceral organs [3-5]. Therefore, the realization of the detection of nitro-aromatic explosives in aqueous phase is very attractive and important [6-10]. Different methods have been developed to detect nitro-aromatic explosives in vapor or solution, such as gas chromatography [11], ion mobility spectrometry [12], electrochemical method [13,14], field-effect transistor and photoluminescence (PL) sensing based on various fluorescent materials (e.g. conjugated polymers) [15-21]. Among them, PL sensing has drawn the most attention for its high sensitivity, stability and easy operation. Because of the strong electron-accepting capacity of nitro-aromatic compounds, the excited states of fluorescent materials could be affected when treating with nitro-aromatic molecules, thus leading to the PL quenching [22,23]. In most cases, the fluorescent conjugated polymers with high PL quantum yield (PLQY) possess low polarity, thus when detecting nitro-aromatic explosives in aqueous media by monitoring the PL, conjugated materials have to face a serious dispersion issue. A lot of efforts have been paid to solve this problem. For example, the occurrence of water soluble conjugated polymeric materials with strong polar groups brought the possibility for aqueous phase PL sensing [24,25]. The preparation of nanoparticles is another effective way, with dispersing fluorescent materials in aqueous media, including small sized conjugated polymers nanoparticles [26,27], carbon-based quantum dots or nanosheets [28,29]. Especially, aggregation induced emission (AIE)-active polymer nanoparticles have been widely used to detect nitroaromatic explosives in mixed organic-aqueous solution or pure aqueous solution for their high

PLQYs in the aggregated state [30-34]. In addition, polymer films with stable crosslinked chemical structure could be used in aqueous media as well [35,36].

Conjugated microporous polymers (CMPs) are promising candidates for the applications in gas desorption [37], heterogeneous catalysis [38], energy storage [39] *etc.*, because of their large specific surface area and multiple reactive sites for molecular recognition [40]. Especially, CMPs exhibited a great potential in the field of fluorescence sensing, due to their good fluorescent property and intrinsic porosity. However, the CMPs synthesized from conventional polymerization methods are normally insoluble powders, which are difficult to process and even more difficult to realize aqueous phase detection. In this work, a CMP poly(triphenylamine-*co*benzothiadiazole)s (PTPABT) nanoparticles with good dispersibility were prepared by Suzukitype coupling $(A_3 + B_2)$ in a toluene/water miniemulsion, followed by dialysis purification to obtain surfactant-free PTPABT nanoparticles. Unlike completely insoluble porous conjugated polymer solids synthesized by conventional Suzuki coupling, the obtained PTPABT nanoparticles with average sizes of 40-70 nm could be readily dispersed in both aqueous and organic solvents. The sensing properties of the PTPABT nanoparticles towards 1,3,5trinitrobenzene (TNB) in pure aqueous media were researched.

2. Experimental

CAUTION! 1,3,5-Trinitrobenzene (TNB) is highly explosive and should be handled carefully only in small amounts.

2.1 General information

The fourier transform infrared spectroscopy (FT-IR) of PTPABT was obtained on a WQF-510A FT-IR spectrometer with KBr pellet as the reference. ¹H NMR spectra were recorded on a Bruker AVANCE 400 or AVANCEIII 600, with tetramethylsilane (TMS) as an internal standard. Atmospheric Pressure Laser Ionization (APLI) measurement was carried out on a Bruker Daltronik Bremen with micrOTOF. Thermal gravimetric analysis (TGA) was undertaken on a TGA/DSC1 STAR System (Mettler Toledo) at a heating rate of 10 °C/min and an argon (Ar) flow rate of 50 mL/min. Nitrogen isotherms were obtained at 77 K on a Micromeritics Tri-star 3000 analyzer. Samples were pretreated by degassing for 12 h at 150 °C. The morphology was observed by field emission scanning electron microscopy (FE-SEM) on a JSM-6700F electron microscope (JEOL, Japan). AFM measurement was performed using a dilnnova microscope from Bruker in the tapping mode at room temperature under ambient conditions. An ALV/CGS-3 light scattering spectrometer equipped with an ALV/LSE-7004 multiplet digital correlator was used in the Dynamic Light Scattering (DLS) measurement. UV-visible absorption spectra were recorded on a Jasco V-670 spectrometer, and PL spectra on a HORIBA Scientific FluroMax-4. The PLQY of PTPABT dispersion was measured with an integrating sphere. The HOMO (highest occupied molecular orbital) levels were estimated on a Surface Analyzer MODEL AC-2 on RIKEN, given as the threshold where photoelectron emission first occurs.

2.2 Materials

All chemicals and reagents were used as received from commercial sources without further purification. The water used throughout all experiments was purified through a Millipore system. The used organic solvents were purified according to standard procedures.

2.2.1 Synthesis of PTPABT nanoparticles

2.2.1.1 Synthesis of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine

1.93 g (4.00 mmol) Of tris(4-bromophenyl)amine was dissolved in anhydrous tetrahydrofuran (THF) (60 mL), the solution was degassed and stirred at -78 °C. 4.86 mL (13.61 mmol) Of *n*-butyllithium solution (*n*-BuLi, 2.8 M in hexane) was added to the above mixture under Ar atmosphere and the resulting solution was stirred for 2 h at -78 °C. 5.83 mL (28.58 mmol) Of 2-

isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added to the solution and the mixture was kept at -78 °C for another 1 hour and then stirred at room temperature for 48 h. The reaction was quenched with water, and the organic layer was extracted with dichloromethane (DCM). After dried over MgSO₄, the solution was concentrated and the solvent mixture of DCM/hexane (3:2) was used as eluent for silica gel column chromatography to isolate the product. The obtained product was further purified by recrystallization from chloroform (CHCl₃)/ethanol to give a white solid in 55% yield. ¹H NMR (600 MHz, C₂D₂Cl₄): δ (ppm) 1.30 (s, 36H), 7.03 (d, 6H), 7.64 (d, 6H). MS (APLI): *m/z* calcd 623.3778; found 623.3667.

2.2.1.2 Synthesis of PTPABT nanoparticles by Suzuki-type coupling in miniemulsion

187 mg (0.30 mmol) Of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine, 132 mg (0.45 mmol) of 4,7-dibromobenzo[c][1,2,5]thiadiazole and 10 mg (0.009 mmol) of tetrakis(triphenylphosphine) palladium(0) (Pd(PPh₃)₄) were dissolved in toluene (20 mL). 248 mg (1.80 mmol) Of K₂CO₃ and 200 mg (0.69 mmol) of sodium dodecyl sulfate (SDS) were dissolved in water (2 mL) with stirring and sonification. The aqueous phase was then added to the organic phase and the mixture was ultrasonicated for 2 min to prepare a stable miniemulsion. Afterwards, the miniemulsion was heated at 85 °C under Ar atmosphere for 24 h. The obtained red dispersion was stirred open to air for 1 day to evaporate toluene and then dialyzed in deionized water for 15 days to remove the surfactant and unreacted monomers using a semi-permeable dialysis membrane with a cutoff of average M_n 3500 g/mol.

To obtain solid PTPABT for characterization, the orange dispersion after polymerization was poured into a saturated NaCl aqueous solution, and $CHCl_3$ and ethanol were added to the mixture. The organic layer was separated and concentrated by rotary evaporation. The residue was precipitated into methanol and finally the solid was collected by centrifugation. The yield is 85%.

2.2.2 Synthesis of PTPABT solid powder by conventional Suzuki coupling

187 mg (0.30 mmol) Of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine, 132 mg (0.45 mmol) of 4,7-dibromobenzo[c][1,2,5]thiadiazole, 0.69 g (5 mmol) of K₂CO₃ and 16 mg (0.014 mmol) of Pd(PPh₃)₄ were dissolved in toluene (7.5 mL) and water (2.5 mL). The mixture was degassed and then heated at 95 °C for 24 h. The precipitate was collected by filtration and washed with water, methanol, acetone and DCM, respectively. Finally the obtained red solid was washed by Soxhlet extractor with methanol, acetone, ethyl acetate and DCM for 1 day each, respectively. The yield for PTPABT powder is 90%.

3. Results and discussion

3.1 Synthesis and characterizations

Herein, we prepared well-defined nanoparticles by Suzuki-type polymerization in miniemulsion followed by dialysis treatment, as shown in Scheme 1. Tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine obtained the treatment of was by tris(4bromophenyl)amine with an excess of n-BuLi followed by the addition of 2-isopropoxy-4,4,5,5tetramethyl-1,3,2-dioxaborolane. 4,7-Dibromobenzo[*c*][1,2,5]thiadiazole was synthesized according to the reported procedures [41]. The Suzuki-type polymerization was controlled between monomer A₃, tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine, and monomer B_2 , 4,7-dibromobenzo[c][1,2,5]thiadiazole in a water/toluene miniemulsion, with Pd(PPh₃)₄ as the catalyst, K₂CO₃ as the base and SDS as the surfactant, respectively. The two compounds (A₃ and B₂) were chosen as the monomers for the polymerization because of their intrinsic crosslinking ability and good fluorescence nature as building blocks. After the reaction at 85 °C for 24 h, stable PTPABT nanoparticles dispersion could be obtained. Dialysis treatment in deionized water was applied to purify the product and resulted in stable aqueous dispersion

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with uniform nanoparticles. It is worthy to note that the obtained nanoparticles could be dispersed not only in water but also in common organic solvents, such as THF, DCM and CHCl₃ *etc*.



Scheme 1. Synthesis route to nanoparticles composed of triphenylamine-based porous polymer PTPABT.

The conventional Suzuki polymerization in toluene for PTPABT was also done with the same monomers for comparison. In the miniemulsion polymerization, there were no solid precipitates even after the reaction at 85 °C for 24 h. However, red precipitates were observed in ca. 3 h in the conventional Suzuki polymerization, and more precipitates emerged with increasing polymerization time. The reaction of the used monomers $(A_3 + B_2)$ results in the polymer chains with crosslinked structure, which would precipitate from the toluene solution when the aggregates become big enough. The obtained crosslinked polymer powder could not be dissolved or dispersed in common organic solvents, thus limiting the application in PL sensing as film or in solution.

The structure of PTPABT was determined by FT-IR measurement. As shown in Fig. 1, PTPABT nanoparticles and PTPABT powder show almost identical peaks, demonstrating the similar chemical structures with different polymerization methods. The peaks at 1592, 1507 and 1474 cm⁻¹ come from the C=C stretching of the phenyl rings, while the C-H stretching of the phenyl rings occurs at 1264, 1184, 1087, 817, 654 and 585 cm⁻¹. The peaks at 1352 and 1317

cm⁻¹ are attributed to the C-N vibration of aromatic tertiary amine. And the S-N vibration occurs at 882 cm⁻¹.



Fig. 1. The FT-IR spectra of PTPABT nanoparticles and PTPABT powder.

Further characterization of PTPABT nanoparticles was carried out by ¹H NMR measurements. The ¹H NMR spectra of the two monomers and PTPABT in 1,1,2,2-tetrachloroethane- d_2 (C₂D₂Cl₄) were shown in Fig. 2. The two monomers show clear chemical structure with exact assignments of hydrogen atoms from their ¹H NMR spectra. As for the polymer, ¹H NMR spectrum is complicated compared with the monomers, because of the highly crosslinked chemical structure. Importantly, it is necessary to note that there are no obvious signals of the monomers in the spectrum of PTPABT, thus demonstrating the successful preparation of polymer PTPABT nanoparticles.



Fig. 2. The ¹H NMR spectra of the two monomers and the polymer PTPABT nanoparticles in $C_2D_2Cl_4$.

3.2 Thermal property

In order to investigate the thermal stability property of the obtained polymer nanoparticles, TGA of PTPABT nanoparticles was measured under Ar atmosphere. There was no obvious decomposition before 250 °C and a 6% weight loss occurred at the temperature of 329 °C. These data demonstrate the good thermal stability of the crosslinked PTPABT framework, which is important for the practical application.

3.3 Porous structure

The surface areas were measured to confirm their porous structures. As shown in Fig. 3, N_2 sorption isotherms were carried out at 77 K. The Brunauer-Emmett-Teller (BET) surface areas of PTPABT nanoparticles and powder from N_2 physisorption are 66 and 32 m²/g, respectively and the pore volumes are 0.31 and 0.20 cm³/g, respectively. The pore size of PTPABT nanoparticles have been obtained to be ca. 1.46 nm. These results demonstrate the CMP nanoparticles have been obtained. The final surface areas are not high because of the structures of the monomers, however,

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the obvious increase of surface area of the PTPABT nanoparticles compared with the powder from conventional polymerization demonstrates that it is beneficial to obtain porous structure *via* the miniemulsion method, because much denser structures may be generated in the process of crosslinking polymerization in the organic solvent.



Fig. 3. The nitrogen adsorption/desorption curves of PTPABT (a) nanoparticles and (b) powder samples at 77 K. Inset shows the pore width distribution profile of PTPABT nanoparticles.

The morphology of PTPABT nanoparticles was assessed by SEM and AFM measurements. The PTPABT dispersion was deposited on a silicon plate for SEM (Fig. 4a). The SEM image demonstrates well-defined nanoparticles have been obtained. At the same time, a thin film was obtained by spin-coating PTPABT dispersion on a quartz plate and used for AFM. The 3-dimensional AFM image is shown in Fig. 4b, which indicates a 3-dimensional graph of the nanoparticles covered surface over an area of 5 μ m × 5 μ m. The diameters of the obtained nanoparticles range from 40 to 70 nm. Fig. 4c shows the DLS characterization of PTPABT nanoparticles, and the average hydrodynamic radius (R_h) was measured as 42.2 nm.



Fig. 4. (a) SEM image of PTPABT nanoparticles. (b) 3-Dimensional AFM image of PTPABT nanoparticles spin-coated on a quartz plate. (c) The hydrodynamic radius distribution of PTPABT aqueous dispersion.

3.4 Photophysical properties

The UV-visible absorption and PL spectra of PTPABT nanoparticles in aqueous solution are shown in Fig. 5a. The maximum absorption peak locates at 323 nm and there is a broad absorption band around 483 nm, which are corresponding to the TPA and BT structures, respectively. The solution shows red emission peaking at 617 nm, due to the complete intra-molecular energy transfer from TPA to BT. The UV-visible absorption and PL spectra of PTPABT film are shown in Fig. 5b. The film shows similar absorption and PL emission with that in aqueous solution, with a slight red shift in absorption and a broader PL spectrum, which can be attributed to the aggregation of the nanoparticles in the solid state.



Fig. 5. The normalized UV-visible absorption and PL spectra of PTPABT (a) in aqueous solution (0.03 mg/mL, excitation wavelength for PL: 483 nm) and (b) as film (excitation wavelength for PL: 483 nm).

PTPABT owns the intra-molecular charge transfer (ICT) characteristic because of its typical donor-acceptor chemical structure, which is demonstrated by the obvious solvatochromism for PTPABT nanoparticles as shown in Fig. 6. The emission gets red-shifted as the solvent permittivity increases, with the maximum PL wavelength from 612 nm in toluene to 670 nm in acetone, and the corresponding full width at half maximum also increases from 118 nm in toluene to 179 nm in acetone.



Fig. 6. The normalized PL spectra of PTPABT nanoparticles in different solvents (excitation wavelength for PL: 483 nm).

3.5 Explosive detection based on PTPABT nanoparticles

For the good dispersion of the obtained fluorescent CMP nanoparticles in pure aqueous solution, polymer PTPABT nanoparticles show a possible application for the detection of nitroaromatic explosives in aqueous media. The aqueous PTPABT dispersion was diluted to a concentration of 0.03 mg/mL for carrying out the PL sensing towards TNB. The PL quantum yield of the PTPABT nanoparticles aqueous solution was determined to be 0.55% with an integrating sphere. Different amounts of TNB (0.05-2 μ mol) were added into the PTPABT aqueous solution (0.03 mg/mL, 2 mL), and the PL emissions were recorded with an excitation wavelength of 480 nm, as shown in Fig. 7a. The emission intensity of the PTPABT aqueous dispersion decreases progressively with the increasing content of TNB. The limit of detection was calculated to be 1.9×10^{-5} M [42]. It is noteworthy that as the content of TNB increases, the PL spectra are blue-shifted from 617 nm (0 mol TNB) to 596 nm (1 μ mol TNB) while the intensity decreases. In contrast, pure THF was added into the solution and no blue-shift in the PL spectra occurred. Therefore, the blue-shift in the sensing experiment may be attributed to the interaction between PTPABT nanoparticles and TNB molecules.



Fig. 7. (a) Evolution of emission spectra of PTPABT dispersion (0.03 mg/mL in 2 mL water) with increasing amounts of TNB. The content of TNB from top to bottom is 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0 and 2.0 μ mol, respectively. (b) Stern-Volmer plots of PL intensity (I₀/I-1) of PTPABT dispersion *vs*. TNB concentration of 0.025-0.45 mM.

The PL quenching of PTPABT dispersion towards TNB shows a linear response in the Stern-Volmer plots in the range of 0.025-0.45 mM with a correlation coefficient R square of 0.9963. A linear regression equation of $(I_0/I) - 1 = -0.30 + [1.22 \times 10^4] C_{TNB}$ is obtained (Fig. 7b). The Stern-Volmer quenching constant K_{sv} is high among the PL sensing towards the explosives in water [27,43-51]. The electron-rich TPA moities in polymer PTPABT and the porous spherical structure of the polymer nanoparticles are beneficial for the interaction of PTPABT with TNB explosive and the diffusion/transport of the TNB analyte inside the polymer nanoparticles, thus leading to the high sensitivity in TNB detection.

Actually, few reports have focused on red-emissive materials for nitro-aromatic explosives detection. Since the basic working principle for PL sensing towards nitro-aromatics is the charge transfer from the LUMO of sensing materials to that of explosives, most of the sensing materials own much higher LUMO than the explosives, and the corresponding band gaps usually result in blue or green emission. For the sensing mechanism based on PTPABT dispersion, there is no overlap between the absorption spectrum of TNB and the emission spectrum of PTPABT aqueous dispersion (Fig. 8a), indicating the PL quenching is not attributed to Förster-type energy transfer between PTPABT and TNB. On the other hand, the HOMO of PTPABT was estimated to be *ca.* -5.4 eV (AC-2 method), and combining the optical band gap (2.2 eV) from the onset of its UV-visible absorption, the LUMO of PTPABT is calculated to be *ca.* -3.2 eV, which is very close to that of TNB (-3.1 eV). Since there is no big barrier between the LUMO of conjugated polymer PTPABT and electron-deficient explosive TNB analyte, it is considered that the photo-

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induced electron transfer could easily happen between PTPABT and TNB (Fig. 8b), which would hinder the radiative transition of PTPABT, thus resulting in an effective fluorescence quenching [52-56].



Fig. 8. (a) Normalized absorption spectrum of TNB and PL spectrum of PTPABT aqueous dispersion. (b) Schematic representation of the excited state electron-transfer process from PTPABT to TNB.

To test the onsite detection of nitro-aromatic explosives based on PTPABT nanoparticles, paper strips with the deposits of PTPABT were prepared by dipping the filter paper into the PTPABT dispersion, followed by drying them in air. The original test paper and the papers after dropping TNB solution with different concentrations under UV irradiation are shown in Fig. 9. When a TNB solution (concentration: 0.001, 0.005, 0.01, 0.05, 0.1 and 0.2 mg/mL, respectively) was dropped onto the test paper, the fluorescence of the PTPABT paper was quenched progressively. Importantly, the quenching effect can be recognized when TNB concentrations. In addition, the sensing behavior of PTPABT test paper towards TNB vapor was checked as well, with the strip over TNB powder for 5 min. From Fig. 9, it can be seen that the fluorescence of PTPABT was distinctly quenched. Therefore, the obtained PTPABT nanoparticles demonstrated

a great potential for fabricating solid sensor and realizing onsite detection towards nitro-aromatic explosives.



Fig. 9. Paper strips of PTPABT before and after dropping a TNB solution (0.001, 0.005, 0.01, 0.05, 0.1 and 0.2 mg/mL, respectively) and over TNB powder for 5 min.

4. Conclusions

Porous conjugated polymer PTPABT nanoparticles with stable structure and good dispersibility in pure aqueous media were prepared *via* Suzuki-type coupling in a miniemulsion with consecutive dialysis process. The PTPABT nanoparticles display intra-molecular charge transfer excited states with red-emission in aqueous dispersion. The electron-rich TPA units inside PTPABT and stable porous structure make the polymer nanoparticles promising for the detection of electron-deficient nitro-aromatic compounds. PTPABT aqueous dispersion has been used to detect the TNB analyte and exhibits a high sensitivity towards TNB with a Stern-Volmer quenching constant K_{sv} of 1.22×10^4 M⁻¹. This method opens a new way for the fabrication of stable polymer nanoparticles and realizing various sensors in pure aqueous media.

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Declaration of interest

The authors declare no conflict of interest.

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Highlights:

Crosslinked PTPABT nanoparticles were synthesized by Suzuki coupling in miniemulsion.

PTPABT nanoparticles can be well dispersed in both water and common organic solvents.

The uniform PTPABT nanoparticles own stable and porous structure.

The PTPABT dispersion can realize aqueous TNB detection with high sensitivity.

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