Investigation of Pyridine/Propargyl Bromide Reaction and Strong Fluorescence Enhancements of the Resultant Poly(propargyl pyridinium bromide)

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S *Supporting Information*

ABSTRACT: Poly(propargyl pyridinium bromide), a kind of conjugated polyelectrolyte with polyacetylene as the backbone and pyridinium as side groups, was synthesized simply via reaction between pyridine and propargyl bromide under mild conditions. The resultant polymer was characterized by ^{1}H NMR, elemental analysis, FT-IR, and GPC-MALLS. An alkyne group was confirmed as the end group of the polymer chains by the alkyne/azide click chemistry, which reveals that the polymerization is terminated by the reaction between propargyl bromide and carbon anions. It is known that monosubstituted polyacetylenes reported have very weak fluorescence intensities, which limit their applications. As a monosubstituted polyacetylene, the freshly prepared poly(propargyl pyridinium bromide) also has a very weak fluorescence. However, we confirmed that addition of some anions to the polymer solution in DMF or DMSO leads to the fluorescence enhancements up to 25 times. Besides, heating the polymer solution at a temperature between 70 and 130 °C for longer than 0.5 h greatly enhanced the fluorescence intensity. The interaction with the anions or the heating enhances the effective exciton confinement within the conjugated backbone and thus results in the fluorescence enhancements. After the fluorescence enhancements, poly(propargyl pyridinium bromide) has relatively strong fluorescence emissions, which will make it promising in fluorescence-based applications.
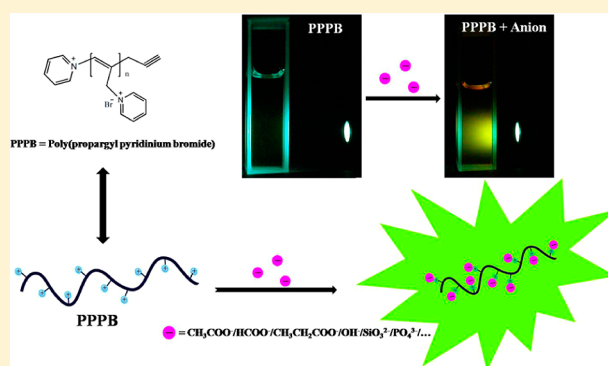
INTRODUCTION

Conjugated polymers featuring a delocalized electronic structure are useful materials for preparing devices such as light-emitting diodes, solar cells, chemo- and biosensors, electrochromic devices, and the devices for organic electronics and nonlinear optics.[1] Polyacetylene (PA) is structurally the simplest one among the conjugated polymers; discovery of the metallic conductivity of the doped PA films in the late 1970s[2−4] led to the 2000 Nobel Prize in Chemistry,[5−7] which is a strong impetus to research on this conjugated polymer. Nevertheless, some drawbacks of PA such as the poor solubility, infusibility, and insufficient stability in air prevent its further commercial application.[8,9] To solve these drawbacks, a number of mono- and di-substituted PAs have been prepared.[8−15] Among substituted polyacetylenes, those with an ionic side group in each repeat unit are polyelectrolyte polyacetylenes (PE-PAs). PE-PAs are attractive, since they are water-soluble, which allows them to be processed by environmental benign methods. In addition, PE-PAs can interact with biological species, which makes them promising in biological applications.

The methods for preparing PE-PAs include post modification of PA's derivatives like poly(6-bromo-hexyne)[16] and direct polymerization of the corresponding substituted monomers.[17−20] In these cases, catalysts were used, and hence, the methods suffer from instability of the catalysts and contamination of the products by catalyst residues. In as early as the 1970s, Kabanov et al. invented a catalyst-free method that could prepare PE-PAs very conveniently. They reported that some propargyl derivatives such as propargyl chloride, propargyl bromide, and alkyl propargyl sulfates could react with some nitrogen-containing compounds directly, without any catalyst or initiator, to produce PE-PAs.[21] In 1991, Blumstein et al. reported preparation of PE-PAs through reacting 2- or 4-ethynylpyridine with alkyl halides.[22] Then, based on the same catalyst and initiator-free method developed by Blumstein's group, several other ethynylpyridine derived PE-PAs were prepared by Gal's group.[23−26] Only a few papers using the

catalyst and initiator free method for preparing PE-PAs have been reported in about 40 years after its invention in 1972.

In our previous study, we reported that simply mixing polystyrene-*b*-poly(4-vinylpyridine) with propargyl bromide in DMF resulted in core−shell nanoparticles containing chromophore within the core.[27] The study reported by Kabanov et al. in 1972 on reaction between pyridine and propargyl bromide to form poly(propargyl pyridinium bromide) was cited to explain the formation of the nanoparticles and the chromophore.[21] While repeating the reaction, we found that it provides a really convenient and low-cost pathway for large scale preparation of the PE-PAs. However, after its invention by Kabanov in the 1970s, no further study on the reaction has been reported and the mechanism is still unclear. Besides, the as-prepared PE-PAs were not sufficiently characterized; we even cannot find in the literature molecular weights of the propargyl derived PE-PAs. Furthermore, propargyl derived PE-PAs are monosubstituted PAs. They, similar to other monosubstituted PAs, have very weak fluorescence. This limits their applications.

In the present study, we selected the propargyl bromide/pyridine reaction in DMF as a representative reaction system to investigate this catalyst and initiator free method based on propargyl derivatives for preparing PE-PAs. The purpose of the present study is to further characterize the resultant polymer and understand the mechanism better, and meanwhile find facile and efficient ways to enhance the fluorescence intensity.

■ EXPERIMENTAL SECTION

Pyridine (Sinopharm Chemical Reagent Co., Ltd., AR) was purified by distillation over sodium under reduced pressure. Propargyl bromide (Shanghai DaRui Fine Chemical Co, Ltd., AR, 98%) was dried over CaH_2 overnight and finally distilled under reduced pressure. *N,N′*-Dimethylformamide (DMF, Shanghai Qiangsheng Chemical Reagent, AR, ≥99.5%) was distilled under reduced pressure after it was dried with $MgSO_4$. 1-Ethylpyridinium bromide (EpB, Tokyo Chemical Industry Co., Ltd., >98%) was used as received. Deoxyribonucleic acid sodium salt from calf thymus (Product Number: D1501) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. All other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., and used without further purification.

^{1}H NMR spectra were recorded on a Bruker DMX400 spectrometer. FT-IR spectra were obtained with a NEXUS-470 spectrometer from Thermofisher. Samples for FT-IR measurement were made by depositing a drop of poly(propargyl pyridinium bromide) (PPPB) solution in DMF on the surface of NaCl flakes and then drying it under a vacuum. A GPC-MALLS system was used to determine the molecular weight of the polymer products, where GPC with two PL mix-D columns was equipped with four detectors (UV−vis, viscosity, refraction index, and multiangle laser light scattering), using DMF with LiBr (2 mg/mL) as eluent at a flow rate of 1 mL/min at 80 °C. The specific refractive index increment (d*n*/d*c*) of PPPB solution in DMF was determined with a JiangKe differential refractometer (JianKe Instrument, Ltd.). Measurement of carbon, oxygen, and nitrogen elements of the samples was conducted on a Vario EL III element analyzer from ELEMENTAR. UV−vis analysis was carried out on a lambda 35 UV−vis absorption spectrometer from Perkin-Elmer. Steady-state fluorescence emission experiments at room temperature were measured on an Edinburgh FLS 920 fluorophotometer with λ_{ex} setting at 482 nm. Lifetime studies were performed on an Edinburgh FLS 920 photocounting system with a hydrogen-

filled pulse lamp as the excitation source (λ_{ex} = 482 nm), and the data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using the software package provided by Edinburgh Instruments. Fluorescence quantum yield (Φ_F) was determined by using rhodamine 6G (Φ_F = 95% in ethanol) as the standard. ITC (isothermal titration calorimetry) measurements were performed on a Microcal VP-ITC system.

Poly(propargyl pyridinium bromide) was synthesized via the following procedures: 1.6 mL (0.02 mol) of pyridine was dissolved in 2.0 mL of DMF in a 20 mL Schlenk flask at room temperature, and then, 1.5 mL (0.02 mol) of propargyl bromide was added to the pyridine solution. The mixture was stirred for about 10 min. The color of the mixture solution changed rapidly from colorless to pink, orange, deep red, and dark brown, successively, accompanied with release of considerable heat. Subsequently, the dark brown mixture was deoxygenated by three freeze−pump−thaw cycles and then the flask was immersed in an oil bath at 60 °C for 100 h. The reaction was terminated by freezing the flask with liquid nitrogen. The products were redispersed in methanol and then precipitated by an excess amount of ethyl ether. After three cycles of redispersion and precipitation, dark brown viscous solids were obtained, which were further purified by extraction using acetone for over 24 h to remove possible residual reactants or the propargyl pyridinium bromide. The final product was dried under a vacuum at room temperature for 24 h. The product was highly hygroscopic and thus stored in a desiccator under a vacuum.

■ RESULTS AND DISCUSSION

In the existing study reporting on preparing poly(propargyl pyridinium bromide) (PPPB) via propargyl bromide/pyridine reaction in methanol, no molecular weights but viscosities of the products were reported.[21] The intrinsic viscosities reported were quite low (0.04 dL/g), so it was thought that the polymerizations occurred inefficiently.[22] It was also reported that the reaction of pyridine with propargyl bromide or propargyl chloride at different feed ratios in acetonitrile or dichloromethane could only lead to mixtures of the pyridinium salt (the quarternization product of pyridine by propargyl bromide or propargyl chloride) and its derivatives rather than poly(propargyl pyridinium bromide) or poly(propargyl pyridinium chloride).[28,29] Actually, high molecular weight is the direct evidence for the polymerization. Therefore, in the present study, the molecular weight of the product is characterized. Gel permission chromatography equipped with detectors of UV−vis and multiangle laser light scattering was used. The molecular weight of PPPB obtained in the present study is as high as $8.8 × 10^4$ (S1, Supporting Information). The relatively high molecular weight of PPPB indicates that the polymerization is successful. In the ^{1}H NMR spectrum of PPPB (Figure 1) in deuterated water, the peak at 5.27 ppm is assigned to protons in conjugated backbones. The three peaks a, b, and c located between 8.0 and 9.0 ppm are signals of a, b, and c H atoms in the pyridinium rings (the inset in Figure 1).[25] In the FT-IR spectrum of PPPB (Figure 2), the signal of C=C bonds of the conjugated backbone of PPPB is detected at 1631 cm^{-1}.[21−26] This evidence confirmed that the polymerization was accompanied by transformation of carbon−carbon triple bonds into the conjugated double bonds, which is similar to the catalyzed polymerization of acetylene. Then, the purified PPPB was analyzed by elemental analysis. The elemental composi-
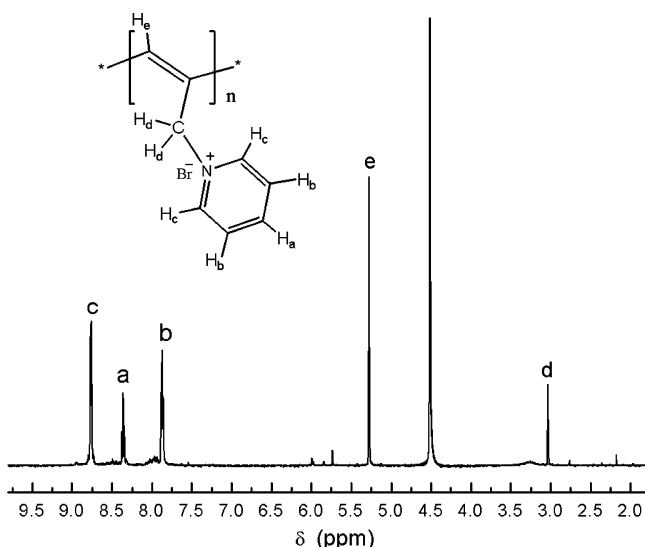
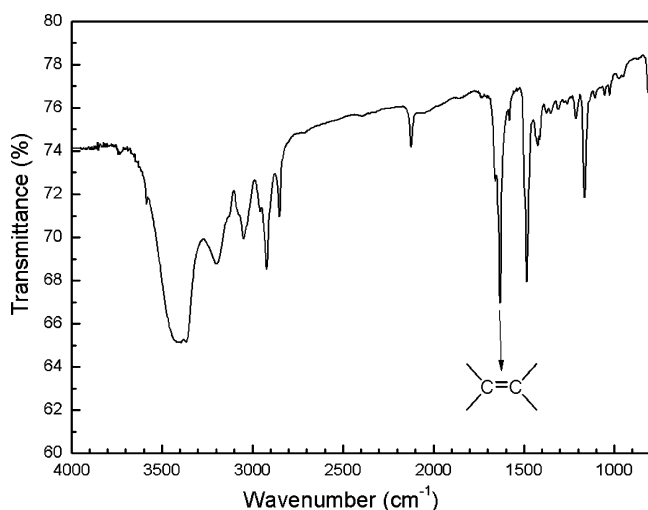**Figure 1.** ^{1}H NMR spectrum of PPPB in deuterated water.

Figure 2. FT-IR spectrum of PPPB.

tions are: C, 47.56%; N, 6.98%; H, 4.38%. Theoretically, three possible structures for the polymer are (1) the homopolymer of propargyl bromide, (2) the copolymer of propargyl bromide and propargyl pyridinium bromide, and (3) the homopolymer of propargyl pyridinium bromide. The elemental analysis results are consistent with the structure that the polymer is the homopolymer of propargyl pyridinium bromide PPPB (the theoretical compositions are C, 48.51%; N, 7.07%; H, 4.08%). It was also confirmed that the change in the pyridine/propargyl bromide feed ratio did not alter the composition of the polymer. Besides, without pyridine, no remarkable reaction

could occur. Therefore, it is concluded that the product resulted from the homopolymerization of propargyl pyridinium bromide, as indicated in Scheme 1.

The mechanism for polymerization of propargyl pyridinium bromide is still unclear. It is notable that the initiation and propagation mechanism for the polymerization of ethynylpyridinium was proposed by Blumstein et al.[22] According to Blumstein et al., the polymerization resulted from the activation of the triple bonds by conjugation of quaternized nitrogen to the α carbon atom; the conjugation stabilizes the carbon anion produced by the nucleophilic attack of the triple bond by pyridine group, and the carbon anions then initiated the anionic polymerization. In the present study, the polymerization resulted from the activation of the triple bonds by the connection of quaternized nitrogen to the α carbon atoms, and pyridine coexisted with propargyl pyridinium bromide. In these two essential aspects, the polymerization of propargyl pyridinium bromide is similar to that of ethylpyridinium. The initiation and chain propagation mechanism can be used for the polymerization of propargyl pyridinium bromide (Scheme 2). However, the termination mechanism for the polymerization of ethylpyridinium was not mentioned by Blumstein. In the present study, the end group of the as-prepared PPPB was confirmed to be alkyne group by the successful azides/alkynes click reaction between the PPPB and azide-terminated poly N-isopropylacrylamide (PNIPAM-N$_3$), which formed the block copolymer PPPB-b-PNIPAM (S2, Supporting Information). This, along with the composition of PPPB measured by the elemental analysis, indicates that the polymerization was terminated by the nucleophilic attack of propargyl bromide by the carbon anions, which capped a PPPB chain with an alkyne group (Scheme 2).

PPPB is molecularly soluble in a polar solvent like water, ethanol, DMSO, or DMF. The photoluminescence spectra of PPPB in the respective solvents, and those in water/DMF mixture solvents at different volume ratios were measured. In all the spectra, PPPB emits a light with a maximum emission peak at about 550 nm, when excited at 482 nm (the concentration of PPPB was 0.2 mg/mL). All the spectra are similar in both the emission range and the position of the maximum emission. Only small differences in fluorescence intensities are observed in the spectra of PPPB in different solvents, as indicated in Figure 3. Using rhodamine 6G in ethanol solution as the standard, the quantum yield of PPPB in DMF is determined to be 1.38%. Similar to other monosubstituted polyacetylenes, PPPB emits fluorescence weakly.

However, it was found that the fluorescence intensity of PPPB in DMF (at 0.2 mg/mL) is greatly enhanced by mixing with sodium acetate. As exhibited in Figure 4, the highest enhancement is obtained at the molar ratio of the pyridinium of PPPB to sodium acetate of 1:1, at which the fluorescence intensity was enhanced 24 times. Further increase in the molar

Scheme 1. Reaction of Pyridine and Propargyl Bromide into Propargyl Pyridinium Bromide and Polymerization of the Latter into PPPB
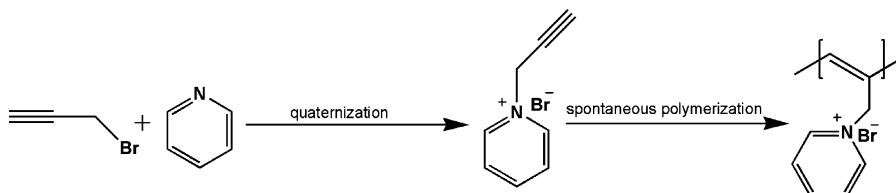
Scheme 2. Mechanism of Polymerization of Propargyl Pyridinium Bromide

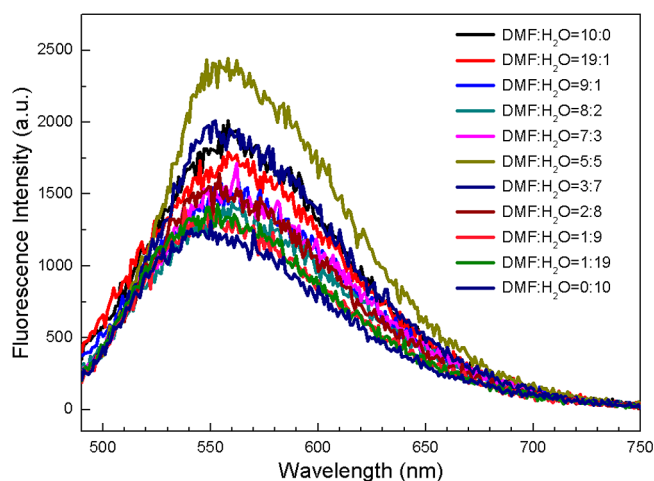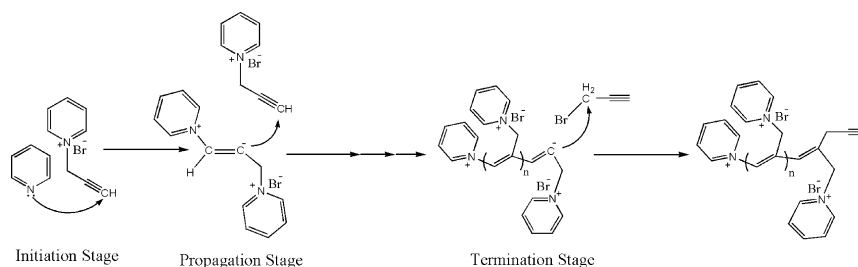Initiation Stage   Propagation Stage   Termination Stage

Figure 3. Fluorescence emission spectra of PPPB in water/DMF mixture solvents at different water/DMF volume ratios at a concentration of PPPB of 0.2 mg/mL.
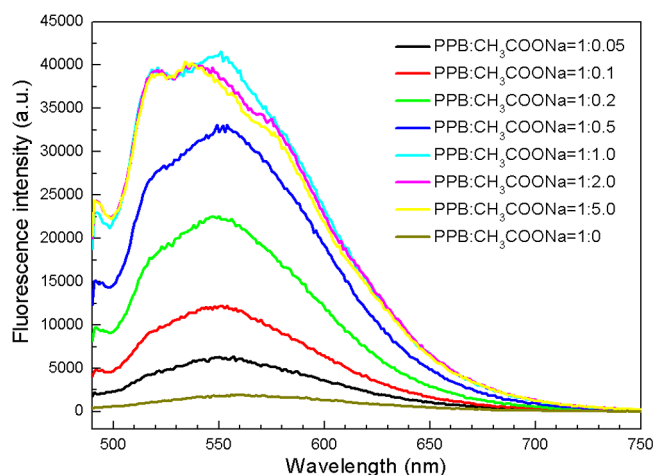

Figure 4. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) mixed with CH_3COONa at different molar ratios of CH_3COONa to PPB. ("PPB:CH_3COONa" in the inset represents the molar ratio of the pyridinium in PPPB to CH_3COONa.)

the mixing. Typically, in a mixture of PPPB with one of the salts at the mole ratio of pyridinium to the salt of 1:1, the water/DMF volume ratio is 1/100. It was confirmed that, when PPPB was solubilized in a water/DMF mixture solvent at a water/DMF volume ratio less than 10%, the addition of sodium acetate into the PPPB solution to give the CH_3COONa/PPB molar ratio of 1:1 can remarkably enhance the fluorescence intensity (Figure 5), and the degree of the enhancement
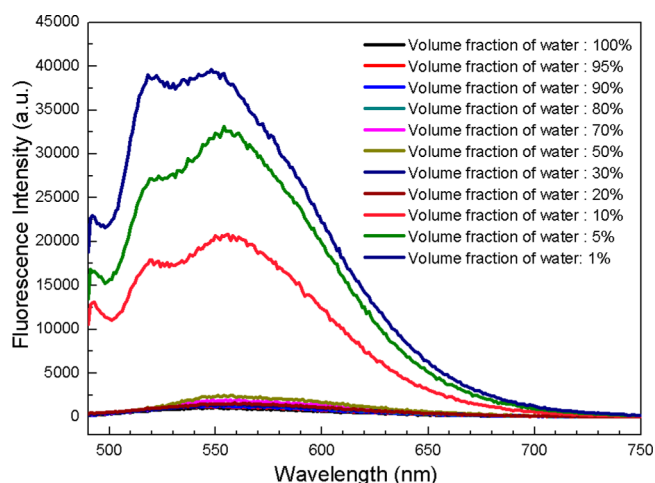

Figure 5. Fluorescence emission spectra of PPPB/CH_3COONa (the CH_3COONa/pyridinium molar ratio is 1:1) in water/DMF mixture solvents at different water/DMF volume ratios (the concentration of PPPB is 0.2 mg/mL).

decreases with the further increase of water content in the mixture solvent. When the solvent is pure water or methanol, no such enhancement by addition of sodium acetate was detected, as explained below.

The light brown color of the PPPB solution in DMF or DMSO becomes deeper after the addition of sodium acetate (S4, Supporting Information). Spectra of UV–vis absorption of PPPB in DMF (0.02 mg/mL) mixed with different amounts of sodium acetate are shown in Figure 6. When the molar ratio of sodium acetate/pyridinium in PPPB solution is less than 1:1, the absorbance increases with the increase of the molar ratio. Maximum absorbance was observed at the molar ratio of the pyridinium groups to sodium acetate of 1:1, which is consistent with the above-mentioned result that maximum fluorescence enhancement was obtained at a molar ratio of 1:1.

As mentioned before, PPPB is the homopolymer of propargyl pyridinium bromide. It is composed of a PA conjugation backbone with $C_5H_5N^+-CH_2-$ as the pendant group (Scheme 1). Without lone pair electrons, the positively pyridinium units cannot complex with positively charged cationic metal ions.[30] Obviously, the fluorescence enhancement
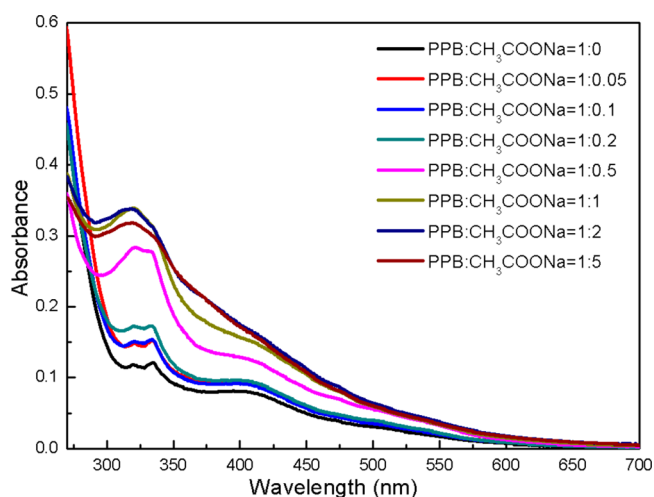
ratio does not affect the fluorescence intensity considerably. Such remarkable fluorescence enhancements by addition of sodium acetate were also observed for PPPB in DMSO (S3, Supporting Information).

It should be mentioned here, due to poor solubility of sodium acetate and the other salts (described below) used for the present study in pure DMF, each of the salts was dissolved in water at a concentration of 0.1 M before its mixing with PPPB in DMF; a small amount of water was introduced during

Figure 6. UV−vis absorption spectra of PPPB in DMF (0.02 mg/mL) without and with addition of CH_3COONa at different pyridinium/CH_3COONa molar ratios.

results from the interaction between sodium acetate and PPPB in the medium. In principle, there are only two possible interactions: (1) The pyridinium groups bind acetate anions through ionic interaction. (2) The π electrons in the PA conjugation backbone may interact with sodium ions. To determine which one is responsible for the fluorescence enhancement, different acetate salts were mixed with PPPB in DMF and DMSO (Figures 7 and 8), respectively. It is observed
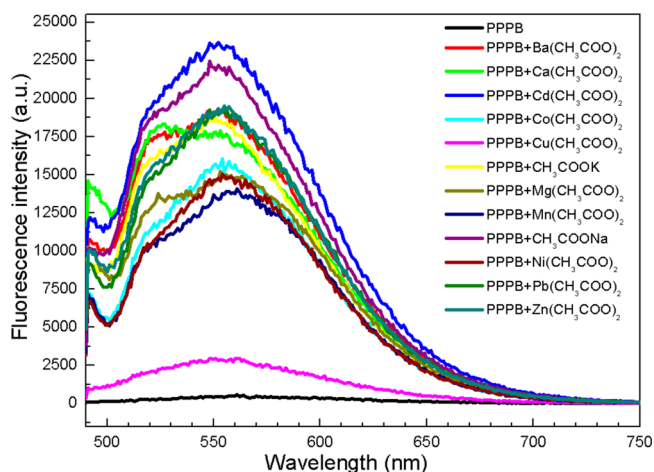

Figure 7. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) mixed with different kinds of acetate salts at a CH_3COO^-/pyridinium molar ratio of 1:1.

that the fluorescence intensity of PPPB in either DMF or DMSO increases after an acetate salt is added, indicating that the binding between pyridinium and acetate anions can enhance the fluorescence intensity; addition of copper acetate leads to the weakest enhancement, since copper ions are known as an effective fluorescence quencher for many conjugated polymers. It is notable that, in the case of the fluorescence enhancement by sodium acetate, sodium cations are inert due to their very weak electrophilicity in the polar medium. Therefore, it is the acetate anions that result in the fluorescence enhancement.
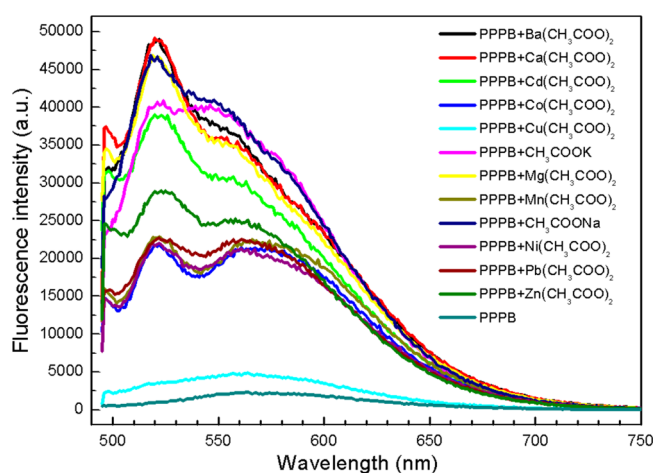

Figure 8. Fluorescence emission spectra of PPPB in DMSO (0.2 mg/mL) mixed with different kinds of acetate salts at the CH_3COO^-/pyridinium mole ratio of 1:1.

Additionally, we confirmed that HCOONa and CH_3CH_2COONa can also greatly enhance the fluorescence intensity of PPPB in DMF (Figure 9). In contrast, the organic
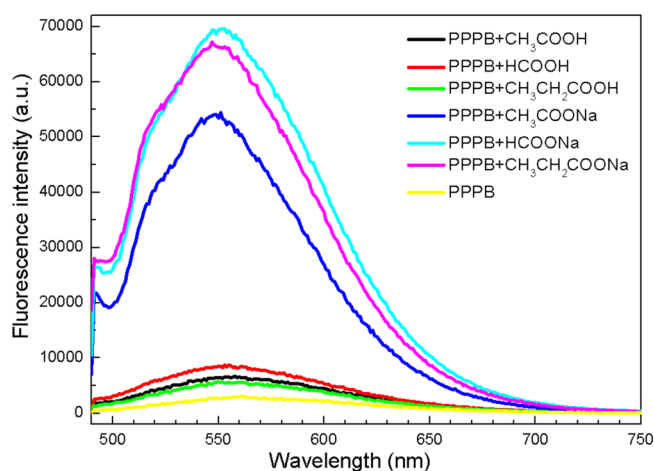

Figure 9. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) mixed with different kinds of aliphatic carboxylic sodium salts and aliphatic acids, respectively, at the mole ratio of COO^- or COOH to pyridinium of 1:1.

acids HCOOH, CH_3COOH, and CH_3CH_2COOH can only affect the fluorescence slightly. Indeed, the interaction occurred between the organic anions and pyridinium cations. An aliphatic acid in DMF should remain largely nonionized. In the system, the aliphatic acids should mainly exist as integrated molecules rather than the ions, and the amount of carboxylic anions in the system is small and the interaction with pyridinium is limited, which is responsible for the small fluorescence enhancements.

The fluorescence intensity of PPPB in DMF could also be enhanced by the mixing with DNA. Due to poor solubility of DNA in pure DMF, DNA was also dissolved in water before the mixing (S5, Supporting Information). The volume fraction of water in the PPPB/DNA mixture solution is 6.6%. As shown in Figure 10, the fluorescence intensity of PPPB is enhanced 10 times at the mole ratio of phosphate to pyridinium of 1:1.
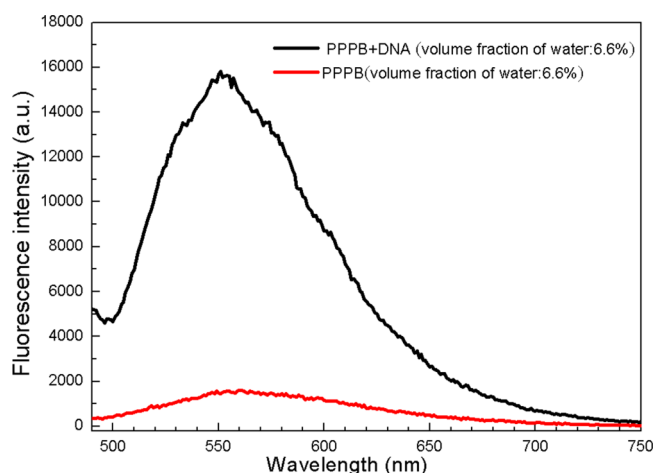
Figure 10. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) mixed with DNA, at the mole ratio of phosphate to pyridinium of 1:1.

Obviously, the interaction between phosphate and pyridinium leads to the enhancement of fluorescence intensity.

The anions other than carboxylic anions can also enhance the fluorescence intensity of PPPB in DMF. As indicated in Figure 11, the fluorescence intensity of PPPB was enhanced 19−25
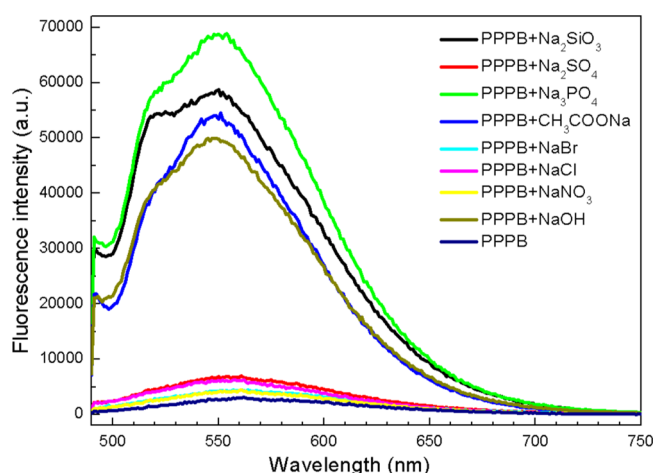

Figure 11. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) mixed with the inorganic anions, respectively, at the pyridinium/anion molar ratio of 1:1.

times by Na_2SiO_3, Na_3PO_4, CH_3COONa, or NaOH. Differently, NaCl, NaBr, $NaNO_3$, or Na_2SO_4 has no apparent enhancement effect on the fluorescence intensity. As mentioned before, the pyridinium/anion interaction is the main cause for the fluorescence enhancements. This is confirmed by the fact that the normalized enthalpy change (ΔH) caused by mixing PPPB with $Mg(CH_3COO)_2$ in DMF at the pyridinium/CH_3COO^{1-} molar ratio of 1:1 is much less than that resulting from mixing PPPB with $MgCl_2$ (or $Mg(NO_3)_2$) in DMF at the identical pyridinium/Cl^{1-} (or pyridinium/NO_3^{1-}) molar ratio; the ΔH values for PPPB/CH_3COO^{1-}, PPPB/Cl^{1-}, and PPPB/NO_3^{1-} in DMF are −5811.3, 38.2, and 179.9 cal/mol, respectively, based on isothermal titration colorimeter (ITC) measurements (S6, Supporting Information). The ITC results demonstrate that the interaction between pyridinium and CH_3COO^{1-} is much

stronger than that between pyridinium and Cl^{1-} (or NO_3^{1-}). Other salts used for the fluorescence enhancements are insoluble in pure DMF, so that water has to be introduced for their mixing with PPPB in DMF. In these cases, the diffusion of water into DMF caused a very large ΔH, which covered the enthalpy change contributed by the pyridinium/anion interaction. As a result, only the interactions between the pyridinium and the salts that are soluble in pure DMF can be measured by ITC. Additionally, the ΔH values for PPPB/CH_3COO^{1-}, PPPB/Cl^{1-}, and PPPB/NO_3^{1-} in water were measured by ITC to be 78.3, 26.5, and 19.4 cal/mol, respectively (S7, Supporting Information). This indicates that the binding between the pyridinium and anions (CH_3COO^{1-}, Cl^{1-}, or NO_3^{1-}) in water is unstable, which should be responsible for the inconsiderable fluorescence enhancements of PPPB in water by mixing with these anions.

The fluorescence enhancements can be recognized by the naked eye. The fluorescence emission photographs of PPPB in DMF and in DMSO with and without mixing with the anions and the corresponding quantum yields are exhibited in S8, Supporting Information.

In principle, there are two possible mechanisms for the fluorescence enhancements: (1) It is known that the pyridinium groups may quench the fluorescence emission through its contact with π electrons of the conjugated backbone.[30] In this case, the interaction between the anions and the pyridinium groups can prevent the contact between the backbone and the pyridinium groups. This enhances the fluorescence, since the quenching by the pyridinium was prohibited. (2) The binding between pyridinium and anions enlarged the size of the side groups, making the conjugated backbone more twisted, resulting in the decrease in efficient conjugation length of the backbone.[11,15] This induces the effective exciton confinement within the conjugated backbone and thus increases the chance of confined excitons to recombine radiatively.[31−34]

Mechanism 1 was excluded by the fact that mixing PPPB with a relatively large amount of 1-ethylpyridinium bromide (EpB) molecules (Scheme 3), which are similar to the pendant

Scheme 3. Chemical Structure of 1-Ethylpyridinium Bromide (EpB)
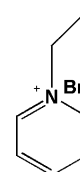
groups of PPPB (Scheme 1), did not affect the fluorescence intensity of PPPB in either the absence (Figure 12) or presence of CH_3COONa (Figure 13) at the pyridinium/CH_3COONa molar ratio of 1:1. Therefore, mechanism 2 is used to explain the fluorescence enhancements. The decrease in the conjugated length was also reflected by the blue shift (in the UV−vis spectra shown in Figure 6) of the absorption peak from 333 to 317 nm induced by mixing with CH_3COONa. Fluorescence enhancement of substituted polyacetylenes due to the steric hindrance effect of the bulky substituents, which could induce exciton confinement in the main chain, was also reported previously.[33,34] The enhanced exciton confinement within the conjugated backbone due to the mixing with anions was
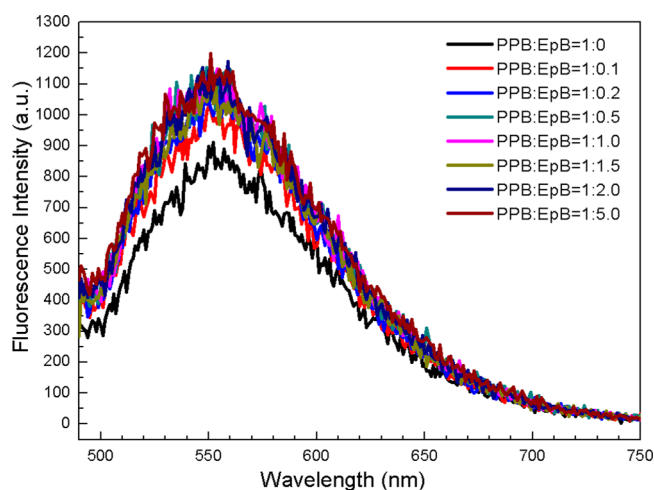
Figure 12. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) mixed with EpB at different EpB/pyridinium molar ratios.

Figure 14. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) heated at different temperatures for 0.5 h.
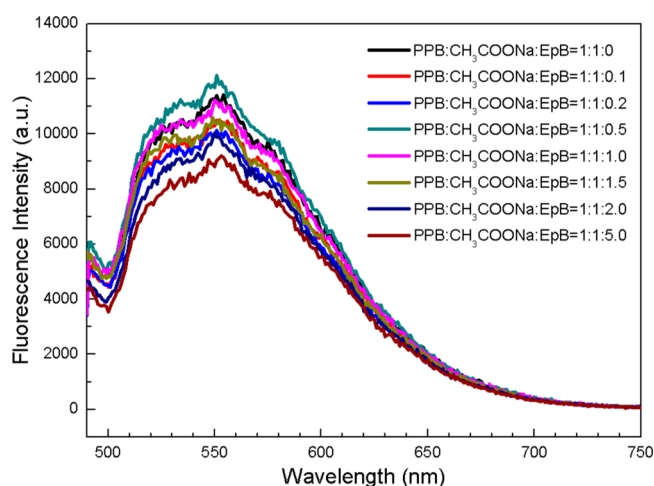

Figure 13. Fluorescence emission spectra of PPPB in DMF (0.2 mg/mL) mixed with EpB at different EpB/pyridinium molar ratios in the presence of CH$_3$COONa (the pyridinium/CH$_3$COONa molar ratio is 1:1).

reflected by the increase in the fluorescence lifetimes (τ). We measured the fluorescence lifetimes of PPPB in DMF mixed with different anions (CH$_3$COO^{1-}, Cl^{1-}, and NO$_3^{1-}$), at a pyridinium/anion molar ratio of 1:1. The results indicated that PPPB in the mixture with CH$_3$COO^{1-} has a longer lifetime (τ = 2.94 ns) than those in the mixtures with Cl^{1-} (τ = 2.32 ns) and NO$_3^{1-}$ (τ = 1.95 ns); the lifetime of PPPB without mixing with anions is 1.70 ns. The relatively long lifetime detected for PPPB in the mixture with CH$_3$COO^{1-} indicates the remarkably enhanced exciton confinement due to the interaction between the pyridinium and CH$_3$COO^{1-}, which is responsible for the fluorescence enhancement.[34]

The fluorescence intensity of PPPB was enhanced 9 times by heating the PPPB solution in DMF at a temperature between 70 and 130 °C for longer than 0.5 h (Figure 14). Before the heating, PPPB was purified; there are no reagents other than PPPB in the system. However, the conformation of the PA backbone could be disturbed by the heating. It is known that σ bonds and π bonds distribute alternatively along a PA backbone, and the efficient conjugation requires that the neighboring p orbitals adopt the same direction (which should
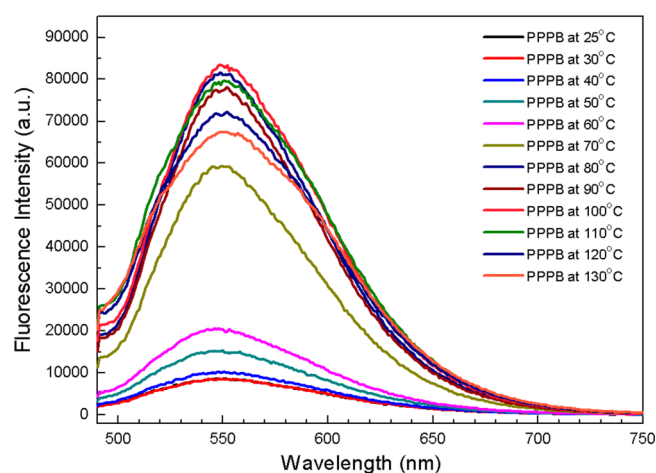
be entropically unfavorable). At a relatively high temperature, the σ bond can rotate around itself and the rotation reduces the conjugation between the two π bonds connected by the σ bonds. Therefore, the heating should result in the decrease in the efficient conjugation length. The remarkable fluorescence enhancements by the heating support the above-mentioned mechanism 2 that the decrease in the efficient conjugation length enhanced the exciton confinement in the conjugated backbone and resulted in the fluorescence enhancement. The fluorescence enhancement by heating is irreversible; when the temperature of the system was cooled down to room temperature, the relatively high fluorescence intensity remained. This is understandable, since the rotation of the σ bonds was restricted at low temperatures; the conformation cannot change back by the rotation of the σ bonds.

■ CONCLUSION

The facile and catalyst and initiator free method to synthesize poly(propargyl pyridinium bromide) (PPPB) via direct reaction of pyridine and propargyl bromide in DMF was reinvestigated. The mechanism for the polymerization was discussed; the mechanism for the initiation and chain propagation was suggested on the basis of the results reported on the similar systems; meanwhile, the chain termination mechanism was confirmed by the alkyne—azide click reaction to form a diblock copolymer containing PPPB as one of the two blocks. The weight-average molecular weight of PPPB was measured for the first time, which is as high as 8.8 × 10^4. Furthermore, the fluorescence intensity of PPPB can be enhanced up to 25 times by mixing with the anions such as CH$_3$COO^{1-}, HCOO^{1-}, CH$_3$CH$_2$COO^{1-}, OH^{1-}, SiO$_3^{2-}$, and PO$_4^{3-}$, respectively, when the solvent is DMF or DMSO. The fluorescence of PPPB can also be enhanced by heating the PPPB solution in DMF at a temperature between 70 and 130 °C for longer than 0.5 h. The enhanced exciton confinement within the conjugated backbone caused by the interaction between the pyridinium and the anions or by the heating is responsible for the fluorescence enhancements. After the fluorescence enhancements, the fluorescence intensity of PPPB is relatively strong, which makes it promising in the applications as probes.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization of the molecular weight of PPPB, synthesis of PPPB-PNIPAM, fluorescence emission spectra of PPPB in DMSO with addition of CH_3COONa, photographs and quantum yields of PPPB without and with addition of anions, mixing DNA with PPPB in DMF, and details on the ITC measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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