

## Synthesis and characterization of poly(3-thiophene acetic acid) upon binding by cationic groups

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### Abstract

Structure, surface properties and morphology of a regioirregular conjugated poly(3-thiophene acetic acid) (PTAA) and four polyelectrolytes based on PTAA with various cations were studied by using FT-IR, <sup>1</sup>H-NMR spectroscopy and SEM. The properties of PTAA and its polyelectrolytes depend on the unique combination of a hydrophobic backbone and hydrophilic ionic side groups. The thermal stability, fluorescence and conductivity properties were investigated. These polymers exhibited fluorescence emissions at about 565 nm characterized for the  $\pi$ -conjugated polythiophene. Undoped polymers have a better conductivity than previous polymers.

**Keywords.** Polythiophenes, conjugated polyelectrolytes, fluorescent properties, conductivity.

### 1. INTRODUCTION

Conjugated polyelectrolytes (CPEs) containing hydrophobic conjugated backbones with hydrophilic groups in the side chains have interesting physical properties and a good solubility in water, creating potential fabrication of these polymers from aqueous solutions and other environment friendly solutions.<sup>[1-7]</sup> As CPEs display both ionic and electronic conductivity, CPEs could be applied as active materials in the progress in electrochromic and other electronic devices, such as organic solar cells, organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs),<sup>[8]</sup> and also applied as novel solid CPEs with improved electrical conductivity.<sup>[9-11]</sup> Another function of CPEs is their utilization as water-soluble sensing agents to detect DNA, protein, small bioanalytes, metal ions, and surfactants. The working principles of these sensors

are based on the changes of UV-Vis and photoluminescence spectra caused by conformational transformations of CPE macromolecules due to their complexation with oppositely charged groups.<sup>[11-16]</sup>

During the last three decades, water-soluble polythiophene derivatives are of special significance among CPEs due to a unique combination of good environmental stability, conductivity and versatility of substituted  $\pi$ -conjugated backbone in various technical applications.<sup>[17-20]</sup> Anionic CPEs based on polythiophene with short alkyl chains has been studied by many scientists.<sup>[21-25]</sup> For example, the first work on CPE published by Wudl Heeger *et al.* in 1987 reported the synthesis and characterization of the conductivity of the films of PTs substituted with ethyl sulfonate and butyl sulfonate side chains.<sup>[26]</sup> McCullough *et al.* showed that the regioregular CPEs with a thiophene ring having a

propionic acid at the 3-position can change from purple to yellow stages by raising the concentration of  $\text{NH}_4\text{OH}$  in aqueous solution.<sup>[27,28]</sup> There have been some studies on poly(3-thiophene acetic acid) but there have been no studies on the properties of water-soluble its polyelectrolytes to have better applicability.<sup>[26,29,36]</sup>

This paper presents the synthesis of poly(3-thiophene acetic acid) (**PTAA**) using oxidative coupling polymerization reaction and properties of four anionic polyelectrolytes derived from **PTAA**. Based on the neutralization reaction with various base solutions at various concentrations, the initial **PTAA** was converted to the respective polyelectrolytes and their properties are reported.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

3-Thiopheneacetic acid, anhydrous iron(III) chloride (98 %), sodium hydroxide, ammonium hydroxide, triethylamine, *N*-methylimidazole (all obtained from Merck) were directly used as collected. Methanol and chloroform were distilled before using.

### 2.2. Synthetic procedure

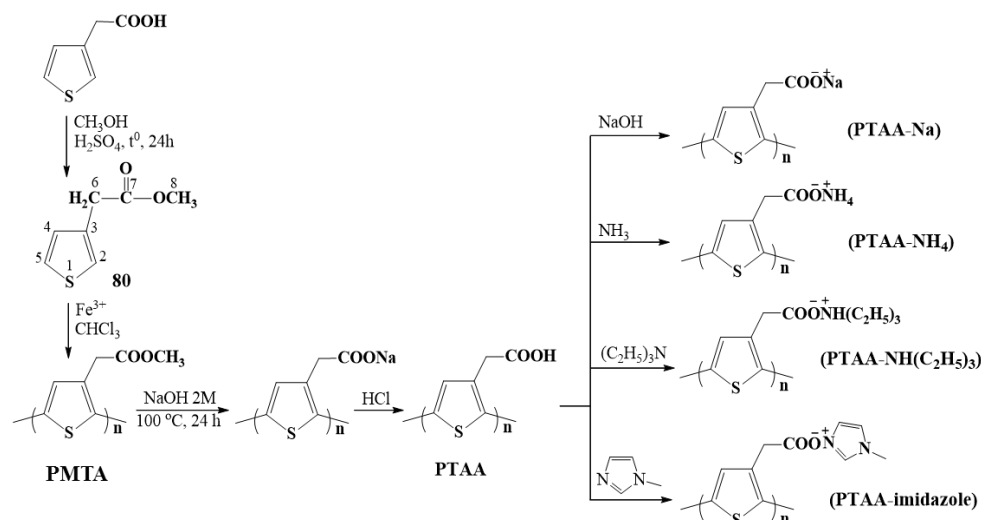
#### Synthesis of methyl 2-(thiophen-3-yl)acetate

3-Thiophene acetic acid (5 mmol) was refluxed in methanol (40 mmol) with 2-3 drops of concentrated  $\text{H}_2\text{SO}_4$  for 24 hours, to prevent extensive oxidative decomposition of the  $-\text{COOH}$  group through polymerization. The excess of methanol was removed by evaporation, and the solution was extracted three times using diethyl ether. The organic extract was washed with deionized water

several times and dried over anhydrous  $\text{MgSO}_4$ . The result solution was evaporated in rotary vacuum at room temperature to get methyl 2-(thiophen-3-yl)acetate (90 % yield). IR ( $\text{cm}^{-1}$ ): 3104, 2999, 2952 (C–H), 1735 (C=O), 1536 (C=C thiophene), 1202, 1152 (C–O–C).  $^1\text{H-NMR}$  [ $d_6$ -DMSO,  $\delta$  (ppm),  $J$  (Hz)]: 7.32 dd  $J_{4-2} = 1.0$ ,  $J_{5-2} = 3.0$  ( $\text{H}^2$ ); 7.03 d  $J_{5-4} = 5.0$  ( $\text{H}^4$ ); 7.47 dd  $J_{2-5} = 3.0$ ,  $J_{4-5} = 5.0$  ( $\text{H}^5$ ); 3.69 s (2H,  $\text{H}^6$ ); 3.62 s (3H,  $\text{H}^8$ ).

#### Synthesis of poly[(thiophene-3-yl-acetic) acid] (**PTAA**)

Methyl 2-(thiophen-3-yl)acetate (1 mmol) was polymerized using oxidative coupling polymerization in chloroform (50 mL) using 4 equivalents of  $\text{FeCl}_3$  (4 mmol). The reaction mixture was stirred under nitrogen atmosphere at room temperature for 48 hours. The green-black solution containing doped poly[methyl 2-(thiophen-3-yl)acetate] **PMTA** was filtered. To eliminate the residual  $\text{FeCl}_3$  and remaining oligomers, the precipitate was washed with methanol and deionized water many times. As a result, the red polymer powder was obtained with a yield of 80 %. **PMTA** (0.125 gram) was hydrolyzed to eliminate the methyl groups from the polymer side chains by refluxing the polymer in aqueous solution of 2 M  $\text{NaOH}$  (0.5 mL). After 24 hours, the insoluble part was eliminated and the solution was neutralized by gradually adding  $\text{HCl}$ . Poly(3-thiophene acetic acid) **PTAA** was precipitated and filtered out from the reaction mixture. Finally, **PTAA** was washed several times with deionized water and dried in vacuum oven at  $80^\circ\text{C}$  to get a dark red powder (70 % yield). IR ( $\text{cm}^{-1}$ ): 3443 (O–H), 1705 (C=O), 1637 (C=C).  $^1\text{H-NMR}$  [ $d_6$ -DMSO,  $\delta$  (ppm),  $J$  (Hz)]: 7.27-7.33 ( $\text{H}^4$ ); 3.79 ( $\text{H}^6$ ).



Scheme 1: Synthesis of poly(3-thiophene acetic acid) **PTAA** and 4 polyelectrolytes

### Synthesis of 04 polyelectrolytes from PTAA

PTAA (0.14 gram) was dissolved in 10 mL of 0.1N NaOH, and then refluxed at about 60 °C for 2 days. Sodium poly(3-thiophene acetate) (PTAA-Na) was separated from the solution by evaporating water and drying in an oven at 100 °C overnight.

The other neutralization reactions leading to 3 polyelectrolytes (ammonium poly(3-thiophene acetate) PTAA-NH<sub>4</sub>, triethylammonium poly(3-thiophene acetate) PTAA-NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and N-methylimidazolium poly(3-thiophene acetate) PTAA-imidazole) were carried out in the same procedure as the synthesis of the polyelectrolyte PTAA-Na, using PTAA and ammonium hydroxide, triethylamine, and N-methylimidazole, respectively.

IR (cm<sup>-1</sup>): PTAA-Na 1638 (C=C); PTAA-NH<sub>4</sub> 3439 (N-H), 1703 (C=O), 1629 (C=C); PTAA-NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> 3442 (N-H), 1702 (C=O), 1635 (C=C); PTAA-imidazole 3431 (N-H), 1699 (C=O), 1629 (C=C).

### 2.3. Devices and methods

FT-IR spectra was recorded on a Nicolet Impact 410 Fourier Transform Infrared Spectrometer. UV-Vis spectra was determined on a Jasco V670 UV-Vis Spectrophotometer (Japan). The NMR spectra was measured on a Bruker XL-500 Spectrometer using a solvent of DMSO-*d*<sub>6</sub>. SEM analysis was performed using a Nova nano Scanning Electron Microscope 450. Under a heating rate of 10 °C/min from 30 to 600 °C in atmosphere, the thermal stability was determined by thermogravimetric analysis (TGA, Shimadzu Simultaneous Measuring Instrument, DTG-60/60H). The photoluminescent spectra were measured on a Horiba Fluoromax Series (USA). The conductivity of polymers tablets was determined using an Agilent E4980A Precision LCR meter (United States).

## 3. RESULTS AND DISCUSSION

### 3.1. FT-IR spectra

FT-IR analysis was performed for PTAA and 04 polyelectrolytes synthesized from PTAA using different base solutions (figure 1). No shift of the absorption of the C–H bond of the thiophene ring has been observed, since it was obscured by stretching vibrations present in a high frequency region, such as O–H groups. The most characteristic feature was the shift of the C=O peak to lower frequency at 1705 cm<sup>-1</sup>, which was a signal of the transformation of –COOCH<sub>3</sub> groups of PMTA to

–COOH groups, which was also supported by the NMR data (see below).

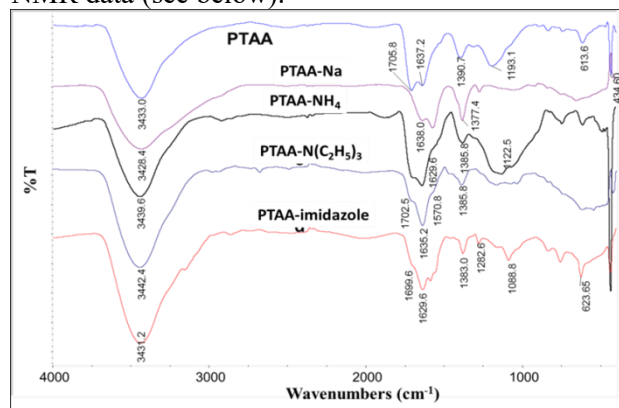


Figure 1: FT-IR spectra of PTAA and 4 polyelectrolytes synthesized from PTAA

The spectra of all polyelectrolytes indicated that the strong shift of the absorption of the C=C–C=C group was presented in the range of 1638–1629 cm<sup>-1</sup>. Moreover, a stronger and broad shift of the absorption of the O–H bonds in the 3500–3000 cm<sup>-1</sup> indicated clearly the good conversion of the carboxylic acid groups of PTAA to carboxylate groups of the polyelectrolytes. Only polyelectrolyte PTAA-NH<sub>4</sub> had a clearly weaker absorption in the 3500–3000 cm<sup>-1</sup> region, which can be explained by the harder transformation of carboxylic group to ammonium carboxylate group.

### 3.2. <sup>1</sup>H-NMR spectra

The <sup>1</sup>H-NMR spectrum of PTAA (figure 2) showed that polymerization has occurred. The signal of the thiophene ring proton was in the range of 7.27–7.33 ppm. The signal (buried in the signal of water) at about 3.79 ppm was characterized by the H<sup>6</sup> proton of the methylene group attached to the thiophene ring. The signal of the proton of the –COOH group was not obvious, only corresponding to a slight bump above 12 ppm.

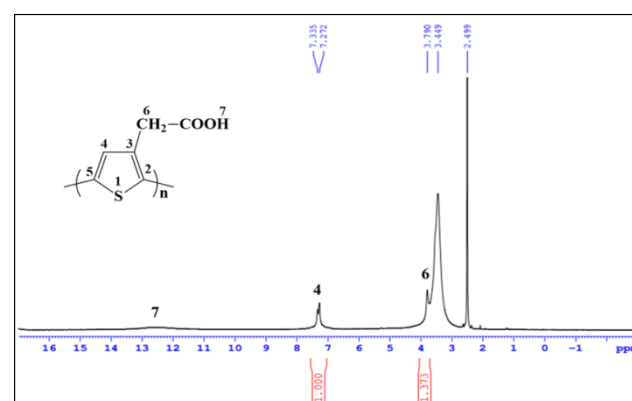


Figure 2: <sup>1</sup>H-NMR spectrum of PTAA

### 3.3. UV-Vis spectra

The UV-Vis spectra and  $\lambda_{\max}$  of synthesized polymers in the solution state and in the solid state were presented in figure 3 and table 1.

Firstly, all polymers had the absorption bands at

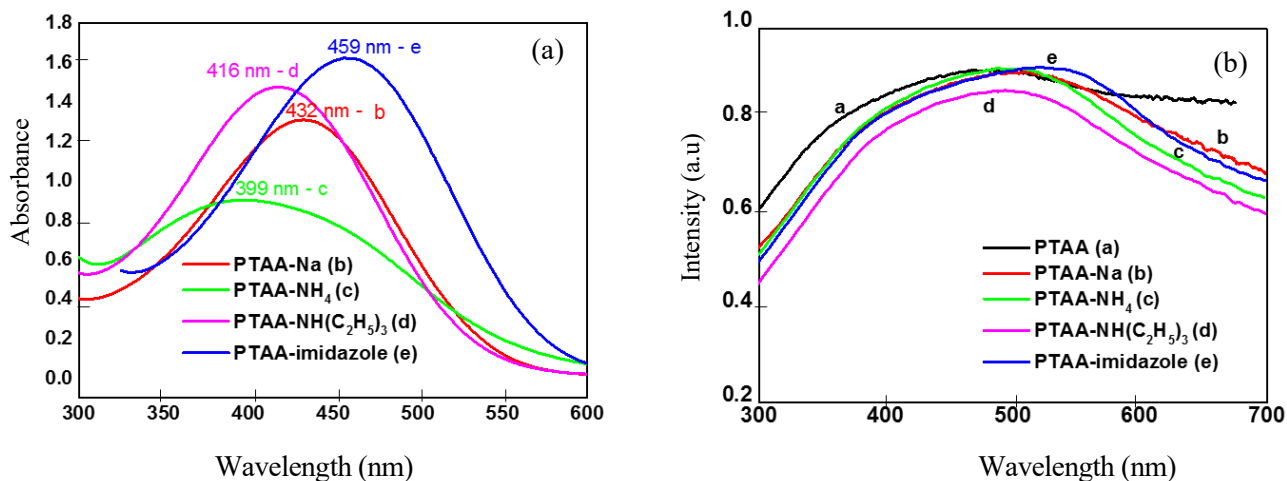


Figure 3: UV-Vis spectra of PTAA and 4 polyelectrolytes synthesized from PTAA in water (a) and solid (b)

Table 1: The absorption bands in UV-Vis spectra of PTAA and 4 polyelectrolytes,  $\lambda_{\max}$  (nm)

Polymer	Solution in water	Solid
PTAA	-	471
PTAA-Na	432	510
PTAA-NH <sub>4</sub>	399	487
PTAA-NH(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	416	492
PTAA-imidazole	459	525

Secondly, the difference in absorption wavelengths of the polymers depended on the charged groups in the polymer solution. PTAA-NH<sub>4</sub> had the shortest  $\lambda_{\max}$  as well as the weakest absorption intensity. Meanwhile, the other 03 polyelectrolytes absorption at wavelengths longer than 17-70 nm depending on the higher concentration of -COO<sup>-</sup> in solution. It can be seen that with increasing basicity of substituents in polyelectrolytes, the absorbance  $\lambda_{\max}$  increased. PTAA-imidazole had the largest wavelength of maximum absorbance. This could be explained that the bulky imidazole aromatic heterocycle of the substituent group increased the polymer conjugated level. According to the McCollough group's study, the UV-Vis absorption spectrum depending on the ions in the solution had also been shown that  $\lambda_{\max}$  of poly[3-(thiophen-3-yl)propionic acid] changed 40 nm when the ion changed from Li<sup>+</sup> to Cs<sup>+</sup>.<sup>[31]</sup>

about 399-525 nm corresponding to the  $\pi \rightarrow \pi^*$  transition in the  $\pi$ -conjugated polythiophene.<sup>[29,30]</sup> In which, the  $\lambda_{\max}$  of 4 polyelectrolytes were higher than that of PTAA. This can be explained that the presence of -COO<sup>-</sup> charged groups lead a better ability to form a coplanar polythiophene backbone.

In solid state (figure 2b),  $\lambda_{\max}$  ( $\pi \rightarrow \pi^*$ ) of polymers had a longer wavelength than that in solution state. This can be explained by the interchain  $\pi$ - $\pi$  stacking interactions<sup>[32]</sup> or the combination of the directional movements of  $\pi$ -electrons and the increase in vibrations of crystal lattice in solid state.<sup>[33]</sup> Compared with the absorption spectrum of poly[(thiophene-3-yl-acetic) acid having  $\lambda_{\max} = 416$  nm,<sup>[29]</sup> the synthesized PTAA had a longer wavelength with  $\lambda_{\max} = 471$  nm based on longer  $\pi$ -conjugation and higher coplanarity of the polythiophene chain.

### 3.4. Morphological characterization

SEM images in figure 4 showed the morphology of PTAA and 4 polyelectrolytes. With all polymers, the morphology was amorphous indicating clearly the regioirregular structure of the polymer chains, which was the usual case for conjugated polymers synthesized by the oxidative polymerization. It should be noted that the morphological structure of all polymers were inhomogeneous, uniform distribution and porous.

### 3.5. TGA analysis

The cationic functional groups of these polyelectrolytes had a major role in thermal stability. Therefore, we performed TGA analyses of PTAA and the polyelectrolytes (figure 5).

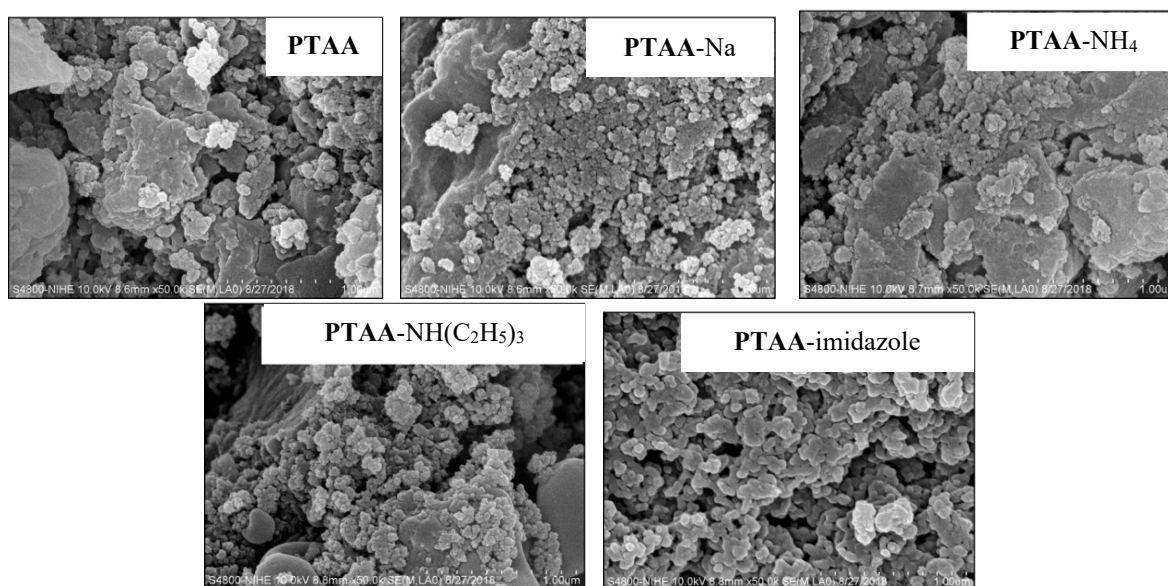


Figure 4: SEM images of PTAA and 4 polyelectrolytes synthesized from PTAA

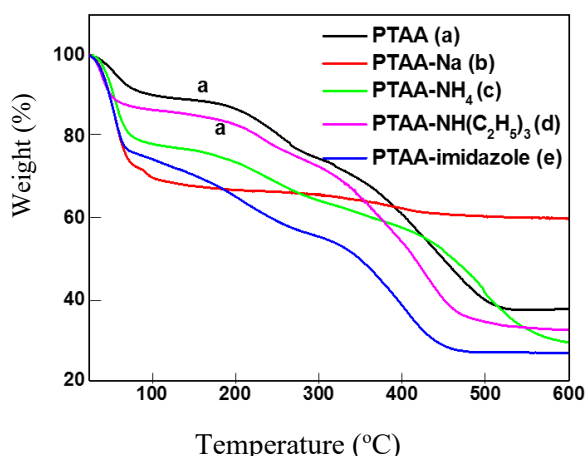


Figure 5: TGA thermograms of PTAA and 4 polyelectrolytes synthesized from PTAA

About 10 % initial weight loss observed up to 100 °C in PTAA could be caused by the release of water in the hygroscopic polymer. PTAA was relatively stable to temperatures as high as 200 °C. A major weight loss occurred at 200 °C to 550 °C where the polymer loses about 60 % of the initial molecular weight. DTA analysis of PTAA showed that the polymer starts to decompose at about 200 °C with the major decomposition between 300 and 480 °C.

The TGA curves of three polyelectrolytes PTAA-NH<sub>4</sub>, PTAA-NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, PTAA-imidazole had nearly the same features as PTAA. It meant that these polyelectrolytes had the same thermal stability properties as initial PTAA; however the initial weight loss of these polyelectrolytes appearing below 100 °C is higher compared to the initial PTAA.

In contrast, the thermal stability of polyelectrolyte PTAA-Na was improved. The remaining weight of PTAA-Na at 600 °C was observed very high, up to 60 % compared to the weight of the initial polymer and other polyelectrolytes. Through comparing the thermal stability, PTAA-Na had the best thermal stability. Probably, the reason was that the formation of -COONa<sup>+</sup> groups could create a crystal structure.

### 3.6. Fluorescence spectra

The fluorescence spectrum of polymers in the solid state was shown in Figure 6b. When replacing the -COOH group in PTAA with the charged groups -COO-X<sup>+</sup>, the fluorescence intensity of polyelectrolytes increased significantly. In which, PTAA-Na had the strongest fluorescence intensity at 565 nm and PTAA-NH<sub>4</sub> had no fluorescence intensity similar to non-luminescent PTAA (table 2).

In the solution state (figure 6a), the initial PTAA had two emission bands at 633 and 690 nm assigned to triplet excitons in the  $\pi$ -conjugated chain.<sup>[34]</sup> However, when the -COOH group in PTAA was replaced by the -COO-X<sup>+</sup> charged groups, there was a shift of the maximum fluorescence emission band to a longer wavelength. With the presence of -COO<sup>-</sup> ion, the conjugated polythiophene was preferentially formed in the coplanar, thereby increasing the fluorescence property. Therefore, the emission band at 630 nm could be assigned to the PTAA, due to the presence of the carboxylic group (-COOH) in the polymer whereas the emission band at 690 nm can be assigned to the polythiophene with

carboxylate group concentration (figure 7). The stronger the base synthesized polyelectrolyte, the

more fluorescence bands of polyelectrolytes tend to shift towards longer wavelengths.

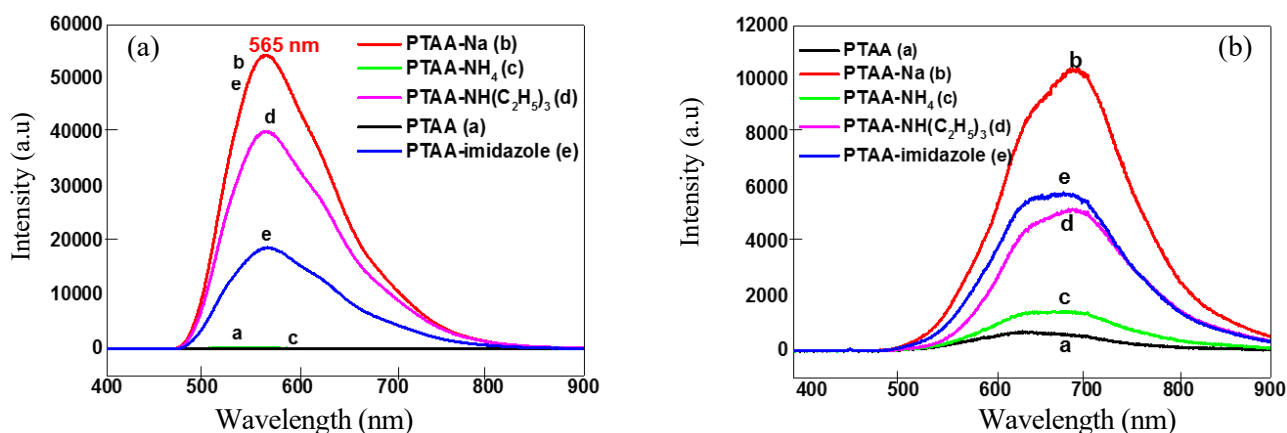


Figure 6: Photoluminescence spectra of PTAA and 4 polyelectrolytes solid (b) and in water (a)

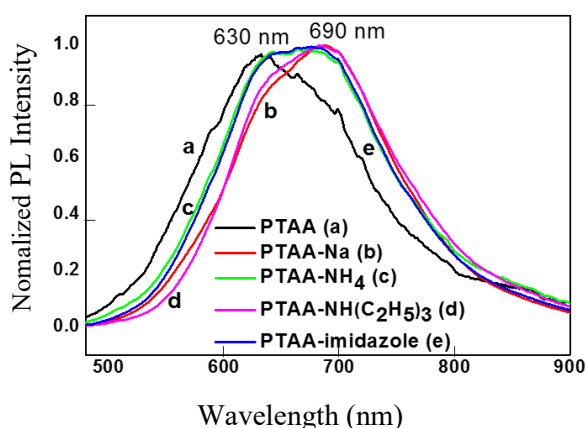


Figure 7: Normalized photoluminescence intensity of PTAA and 4 polyelectrolytes

Table 2: Emission properties of PTAA and 4 polyelectrolytes,  $\lambda_{\max}$  (nm)

Polymer	Solid	Solution in water
PTAA	-	-
PTAA-Na	565	686
PTAA-NH <sub>4</sub>	-	684
PTAA-NH(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	566	684, 644
PTAA-imidazole	569	675, 643

### 3.7. Conductivity property

The conductivity of all polymers tablets of 0.5 cm diameter was shown in Figure 8. According to previous studies, the conductivity of undoped poly[(3-thiophene acetic acid)] was very low with a value of  $1.2 \times 10^{-8}$  S/cm.<sup>[35,36]</sup> The conductivity of the synthesized PTAA ( $1.7 \times 10^{-6}$  S/cm) was about 100 times higher than the previous synthetic PTAA at 1

MHz.<sup>[10,9]</sup> When replacing the -COOH group in PTAA with charge carriers in 3 polyelectrolytes (PTAA-NH<sub>4</sub>, PTAA-NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, PTAA-imidazole), the conductivity of these polyelectrolytes was almost unchanged due to the electricity carrier groups in the form of organic salts. However, the conductivity of PTAA-Na increased sharply to  $7.4 \times 10^{-6}$  S/cm.

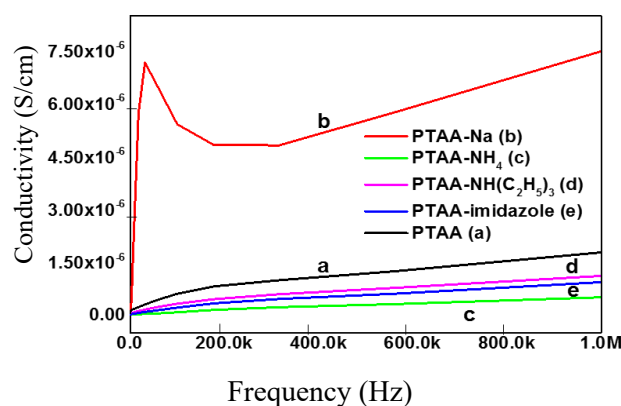


Figure 8: Conductivity of PTAA and 4 polyelectrolytes synthesized from PTAA

### 4. CONCLUSION

PTAA has been successfully synthesized using an oxidative coupling reaction. Based on the results of the TGA, the UV-Vis spectra, the fluorescence spectra and conductivity measurements, the properties of polyelectrolytes with charge-carrying groups had changed significantly compared with the initial PTAA. In which, PTAA-Na had the best thermal stability, best electrical conductivity and the strongest fluorescence intensity at about 690 nm. PTAA-imidazole had the longest absorbance wavelength at about 459 nm (in the solution state)

and 525 nm (in the solid state). The main reason for the difference in properties between polyelectrolytes was the difference in the nature of the positively charged groups and the presence of the  $-\text{COO}^-$  group leading to an increase in the  $\pi$ -conjugation length.

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