

## Biocatalytic Synthesis of Unusually Photoluminescent Oligomers and Electrically Conducting Polymers of 4-(3-pyrrolyl)Butyric Acid

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**ABSTRACT:** Unusually photoluminescent undoped oligomers and doped electrically conducting polymers of 4-(3-Pyrrolyl)butyric acid have been enzymatically synthesized using the oxidoreductase soybean peroxidase as a catalyst. This biocatalytic approach provides a direct route to a fluorescent-undoped oligomer of pyrrole that requires no protection/deprotection chemistry. The synthesis is carried out in aqueous media that requires only monomer, enzyme, and hydrogen peroxide. The undoped oligomer exhibits stable emission properties and is highly sensitive to the presence of environmentally important metal ions, such as Co(II), Hg(II), and Cu(II) in solution. Electrically conducting polymers can also be obtained by adding a dopant to a buffered reaction solution prior to initiating the polymerization. Polymers doped with camphor-10-sulfonic acid exhibit conductivity values as high as  $10^{-2}$  S/cm. Additionally, polymers synthesized in the presence of a biobased cationic template, *N,N,N*-trimethylchitosan chloride, exhibit conductivity values that are an order of magnitude greater than polymers synthesized with the anionic polymeric template, poly(styrene sulfonic acid)-sodium salt. The biobased synthetic strategy described here is the first report of directly obtaining an undoped, fluorescent conjugated oligomer of a pyrrole in aqueous solution. Unlike conventional chemical catalysts, the enzyme does not dope the oligomer and therefore provides the opportunity to directly obtain fluorescent conjugated species. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 41035.

**KEYWORDS:** biosynthesis of polymers; conducting polymers; monomers; oligomers and telechelics; optical and photovoltaic applications; sensors and actuators

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### INTRODUCTION

With the world moving towards increasingly safe, clean, and environmental friendly products, biocatalyzed and bio-inspired synthetic strategies have enormous growth potential in diverse applications. Specially, the use of enzymes and biomimetic catalysts for the synthesis of polymers has shown great promise in response to these demands.<sup>1–3</sup> Recently, more environmentally benign routes have been developed for the synthesis of nonhalogenated flame retardant,<sup>4</sup> anticancer compound,<sup>5</sup> chiral pharmaceutical intermediates,<sup>6</sup> nanomaterials,<sup>7</sup> biomaterials,<sup>8</sup> and electrically conducting polymers.<sup>3</sup>

While environmental considerations may solely justify the use of safer synthetic strategies, enzyme catalysis also provides a unique route to directly produce materials that are not achievable by chemical routes. In the field of advanced materials, the use of enzymes offers several advantages over traditional chemical oxidants or electrochemical polymerization methods. These include slower and more controlled polymerizations, higher selectivity, lower inherent toxicity, and use of safer solvents and more neutral reaction pH conditions. As an example, we have reported the aqueous polymerization of polypyrrole with the enzyme soybean peroxidase results in a highly conductive, more defect free polymer<sup>9</sup> compared with those prepared

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electrochemically<sup>10</sup> or with the chemical oxidant, ammonium peroxydisulfate.<sup>11</sup>

Conjugated polymers (CP) of pyrrole and its derivatives have previously been reported and are promising materials for erodible scaffolds for cells growth,<sup>12</sup> humidity sensors,<sup>13</sup> and biosensors for the detection of DNA hybridization.<sup>14</sup> Notably absent from this list of applications are reports on their use as fluorescence sensors. In comparison, other classes of photoluminescent CPs have been shown to detect chemical warfare agents,<sup>15</sup> nitroaromatic explosives,<sup>16</sup> and heavy metals.<sup>17</sup> Highly fluorescent CPs have traditionally been synthesized using multistep schemes that require organic solvents and transition metal catalysts.<sup>18</sup> Here we report a simpler and environmentally benign approach to conjugated oligomers of pyrrole with photoluminescent properties.

Theoretical studies on polypyrrole and its derivatives have predicted the possibility of photoluminescence for a neutral oxidation state polymer.<sup>19</sup> However, due to their low oxidation potentials, neutral species of polypyrroles readily oxidize in air, resulting in the fluorescence being quenched easily. Therefore, there are only a few reports of fluorescence in polypyrrole.<sup>20–22</sup> It is more common to observe photoluminescence originating as the result of fluorescent side chains in polypyrroles than from the conjugated polymer backbone.<sup>23,24</sup>

Here, we report an enzymatic approach to the oxidative polymerization of a beta-substituted pyrrole derivative, 4-(3-Pyrrolyl)butyric acid (3-BAP). The coupling methodology is simple, environmentally benign, and can be tailored to produce photoluminescent oligomers or electrically conducting polymers of 3-BAP. The reaction is a one pot, aqueous based oxidation catalyzed by soybean peroxidase (SBP). When the reaction is conducted under ideal conditions, containing only monomer, enzyme, and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in unbuffered deionized (DI) water, the resulting material is a unique photoluminescent pyrrole-based oligomer with a stable green emission. The fluorescence of the resulting oligomer can be quenched upon exposure to metals in solution.

Moreover, electrically conducting polymers of 3-BAP can also be obtained, using the same enzyme catalyzed approach, by adding either small molecule dopants or a polymeric template prior to initiating the reaction.

## EXPERIMENTAL

### Materials

4-(3-pyrrolyl)butyric acid (purity 95%), poly(styrene sulfonic acid)-sodium salt (MW = 70,000 Daltons), (±)-camphor-10-sulfonic acid (purity 98%), anhydrous citric acid (purity 99%), sodium citrate monohydrate (purity 99%), chitosan (medium MW, deacetylated), Iodomethane (purity 99%), hydrogen peroxide (30% by weight in water), and dimethyl sulfoxide (purity 99%) were purchased from Sigma-Aldrich, St. Louis, MO. Dilute solutions of H<sub>2</sub>O<sub>2</sub> were prepared to a concentration of 3.4 wt % using DI water and stored in the refrigerator before and after use.

Soybean Peroxidase (SBP) (EC 1.11.1.7) was purchased from Bioresearch Products Inc. North Liberty, IA and obtained as a reddish brown powder. SBP with an RZ (Reinheitszahl value) of

2.8 and a specific activity of 1840 IU per mg dry weight was used for all reported experiments. Specific activity was assessed through an established guaiacol oxidation assay.<sup>25</sup>

DI water was obtained from a Millipore Elix 3 system equipped with Proguard 2 filters. The system produces DI water with a resistance greater than 15 Mohm•cm.

### Methods

**Synthesis of Photoluminescent Oligomers of 3-BAP.** In a typical reaction, 10 mL of unbuffered DI water and 0.5 mmol 4-(3-Pyrrolyl)butyric acid are mixed and bath sonicated for 20 min. The solution is then cooled to 2–4°C. 150 μL of a 10 mg/mL stock solution of SBP is added to the mixture, followed immediately by the addition of a single aliquot (41.6 μL of a 3.4 wt % solution) of H<sub>2</sub>O<sub>2</sub>. Successive aliquots of the same volume and concentration of H<sub>2</sub>O<sub>2</sub> are added every 5 min over the next hour. The reaction is then allowed to stir for an additional 30 min. The final product solution is centrifuged, the solvent decanted, and the remaining solids dried overnight under vacuum at 50°C. Control reactions were conducted in an identical manner, however, without the addition of SBP.

### Synthesis of Electrically Conducting Polymers from 3-BAP.

Electrically conducting polymers of 3-BAP are synthesized in a similar manner but in presence of 0.5 mmol of dopants (small molecules) and in a citric acid buffer at a pH of 3.5. Quantities for all polymeric dopants/templates are calculated based on the molecular weight of the polymer's repeating unit. For polymers synthesized with camphor sulfonic acid (CSA), the final product is isolated in the same manner as the fluorescent oligomer. Polymers synthesized in the presence of polymeric templates, either poly(styrene sulfonic acid, sodium salt) (PSS) or *N,N,N*-trimethylchitosan chloride (TMC), are precipitated in acetone, isolated via centrifugation, and dried overnight under vacuum at 50°C. TMC is synthesized prior to the reaction by reacting deacetylated chitosan and iodomethane according to a previous report.<sup>26</sup>

### Characterization

All products are characterized using an Agilent 8453 photodiode array UV-Vis spectrometer. For absorption measurements of electrically conducting polymers, a 30 μL aliquot of the reaction mixture is diluted with DI water to a total volume of 400 μL in a 1mm quartz cuvette. Absorption measurements of the fluorescent oligomer were obtained in DMSO. Fluorescence measurements are recorded with a Perkin Elmer LS 55 luminescence spectrometer. Quartz cuvettes with path length of 1 cm, were used to record all spectra. Emission spectra are recorded at very dilute concentrations (typically 0.005 mg/mL) to limit self-quenching due to aggregation. Conductivity measurements were taken on pressed pellets of the solids via a four-point probe method after drying in a vacuum oven for 24 h. Conductivity measurements were performed with a Keithley 2750 DMM and a Keithley 6221 source meter. Fourier-transform infrared (FTIR) attenuated total reflectance (ATR) measurements were obtained using a Thermo Scientific Nicolet 4700 with a Smart Orbit ATR accessory.

### *In Situ* <sup>1</sup>H NMR Reaction Monitoring

Initial stage *in situ* <sup>1</sup>H NMR reaction monitoring is conducted using a Bruker 500 MHz NMR. Samples with 3-BAP and SBP

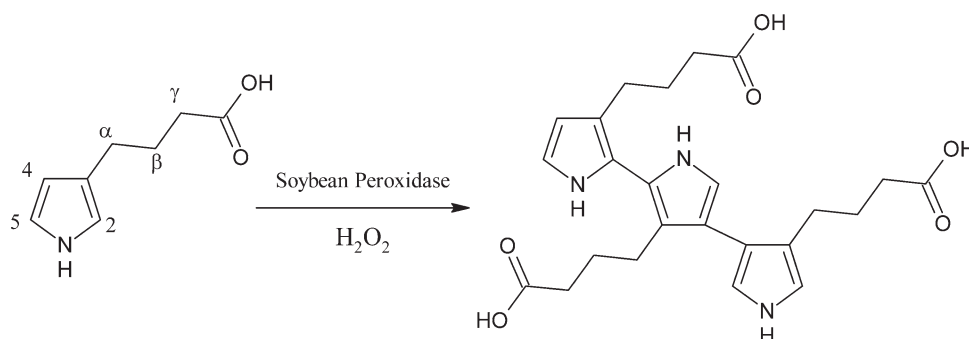


Figure 1. Polymerization scheme of 4-(3-pyrrolyl)butyric acid.

were prepared in 1 mL of deuterated water. All samples were prepared at concentrations comparable with those used in the actual reactions. A  $^1\text{H}$  NMR scan was recorded prior to a single addition of  $\text{H}_2\text{O}_2$  and every few minutes afterwards. Structural comparisons between spectra were made by holding the integration for the protons of the  $\alpha$ -carbon in the butyric acid side chain constant at 2.0, while monitoring changes to the protons at the 2, 4, and 5 positions on the pyrrole ring. Figure 1 presents the structure of the monomer and the overall reaction scheme.

**Metal Ion Sensing.** A stock solution was prepared containing 0.005 mg/mL of the fluorescent oligomers of 3-BAP in dimethylsulfoxide (DMSO). Only samples that were oligomerized in unbuffered DI water without a dopant/template present in the solution were used for sensing applications. Metals and their specific counter ions were selected for their environmental importance and their solubility in DMSO. These included copper(I) tetrakis(acetonitrile) hexafluorophosphate, copper (II) acetate monohydrate, mercury(II) acetate, cobalt(II) acetate tetrahydrate, iron(II) sulfate heptahydrate. For each set of measurements, 3 mL of the stock solution was pipetted into a quartz fluorescence cuvette. To this solution, aliquots of 0.1 mg/mL solutions of metal salts were added. After each addition, the solution was thoroughly mixed and its emission spectrum was recorded.

## RESULTS AND DISCUSSION

### Synthesis and Characterization of an Undoped Luminescent 4-(3-pyrrolyl)Butyric Acid Oligomer (oligo(3-BAP))

Typically, the oxidation/polymerization of conjugated monomers, like pyrrole,<sup>27</sup> aniline,<sup>28</sup> and thiophene,<sup>29</sup> require organic solvents or strong acidic solutions. The use of an enzyme catalyst precludes use of such reaction conditions. In organic media and in very low pH conditions, the activity of peroxidase has been shown to be greatly diminished.<sup>30–32</sup> However, mildly acidic conditions (pH 3.5–5) are an effective polymerization media for the enzymatic synthesis of CPs.<sup>33,34</sup> It is very interesting to note that the oxidative coupling of 3-BAP, when catalyzed by SBP, proceeds smoothly without a template and in unbuffered deionized (DI) water.

Unlike the unmodified pyrrole monomer, where no polymerization is observed in unbuffered aqueous solutions or without the presence of a template, in the case of 3-BAP the polymerization

reaction proceeds. It is hypothesized that the butyric acid side chain helps facilitate the reaction. The acid side chain may serve two purposes during the reaction. First, when 3-BAP is dissolved in deionized water at a concentration of 50 mM, the pH drops to 3.5 due to disassociation of acid side chains; therefore, no additional buffer is needed for the reaction. Second, the side chain may create a “unique local low pH environment” favorable for polymerization similar to the conditions already reported during the enzymatic synthesis of polyaniline.<sup>35</sup>

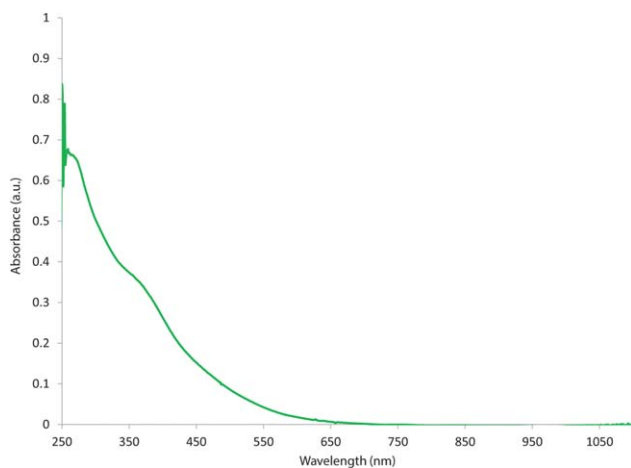
### Monitoring Reaction Progress Using Absorption Spectroscopy

The initial solution for all reactions is slightly pale yellow with a dispersion of gray monomer particles. Upon the addition of SBP and first aliquot of  $\text{H}_2\text{O}_2$ , the reaction solution transitions quickly (within two minutes) through a slight green color to a dispersion of black particles. The particles remain suspended with stirring until the end of the reaction. Upon completion of polymerization, the product is easily isolated via centrifugation. For the control experiments without the addition of SBP, no color change or product formation was observed under identical reaction conditions.

During the reaction, an initial absorption from the 3-BAP monomer is observed at 210 nm. This peak immediately shifts bathochromically upon initiation of the reaction. The final absorption spectrum of the oligomeric product in DMSO has a broad nonstructured feature that spans from 300 to 700 nm, Figure 2. This is consistent with the spectrum of an undoped pyrrole oligomer.<sup>36</sup> The oligomer is sparingly soluble in very basic solution and soluble up to a concentration of 1 mg/mL in DMSO at room temperature. Extending the time to 2.5 h (the optimum reaction time that we have reported earlier for the polymerization of pyrrole with SBP)<sup>9</sup> results in a completely insoluble product.

### In Situ Monitoring of Reaction Progress Using $^1\text{H}$ NMR Spectroscopy

During the reaction, the lack of a template/dopant appears to have an effect on the structure of the final product. Unfortunately,  $^1\text{H}$  NMR of the final products reveal only broad peaks in the aliphatic region corresponding to the side chain of the butyric acid. There are no clearly defined peaks and hence no useful structural information about coupling sites within the pyrrole ring can be obtained from the NMR spectra of the products. This phenomenon has been observed and reported in the  $^1\text{H}$  NMR spectra of other conjugated polymers and more



**Figure 2.** Absorption spectra of Oligo(3-BAP) in DMSO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

specifically with self-doped beta substituted polypyrroles.<sup>37</sup> Therefore, the initial stage *in situ* reaction monitoring was conducted using <sup>1</sup>H NMR.

Figure 3 presents the overlapping <sup>1</sup>H NMRs spectra for the initial stages of the reaction without a template. The spectra show the signal for the protons at 6.65 ppm (2 position on the pyrrole ring) is initially very weak and quickly disappears upon initiation of the reaction. The spectra also suggests that the signal from the proton at position 4 (6.05 ppm) within the pyrrole ring disappears preferentially compared to the 5 position (6.75 ppm). The integration values for the protons at the 4 and 5 positions compared with those present in the butyric acid monomer side chain also supports this observation (Supporting Information).

The data suggests that monomer–monomer coupling occurs at the 2 and 4 positions within the pyrrole ring. This coupling pattern results in a highly sterically strained product due to crowding between adjacent groups. Ultimately, this limits the size of the oligomer formed. Molecular weight characterization via matrix assisted laser desorption/ionization time of flight (MALDI-ToF) mass spectrometry for the undoped product appears to support this argument and reveals the final product to be an oligomer of at least 3 repeat units (Supporting Information). Thermogravimetric analysis also shows the oligomeric product is more thermally stable than the 3-BAP monomer, indicating the presence of at least a few monomeric units coupled together (Supporting Information).

### Characterization of the Oligomer Using Infrared Spectroscopy

The FTIR-ATR spectrum, Figure 4, confirms the characteristic PPy peaks at 1450 and 1540  $\text{cm}^{-1}$  from pyrrole ring stretching in the undoped oligomer. These peaks are clearly present and more pronounced in the oligomer spectrum compared with the monomer. The vibrational bands in the oligomer are broader and less defined compared with the monomer. The carbonyl peak of the butyric acid side chain (1705  $\text{cm}^{-1}$ ) is still strongly

present in the oligomer spectrum indicating that it is unaffected by the reaction.

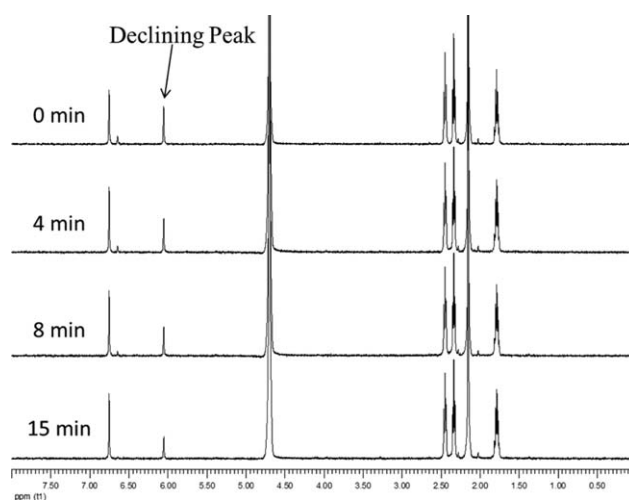
### Characterization of Photoluminescence of Oligomer of 3-BAP Using Fluorescence Spectroscopy

One of the most interesting characteristics of the oligomer is the stable photoluminescence. To the best of our knowledge this is the first report of photoluminescence from oligopyrrole. The photoluminescence properties of the 3-BAP oligomer are studied in DMSO. Figure 5 presents the oligomers emission spectrum upon excitation at 350 nm. The undoped oligomer exhibits an emission maximum at 433 nm with a shoulder at 500 nm. Excitation at 375 nm also provides a similar spectrum. Emission from solutions stored for up to 6 months show little change, indicating the oligomers are quite stable and exhibit little or no deleterious effects upon exposure to air even for a prolonged duration of time. Quantum yield calculations for the undoped oligomer are currently ongoing and will be reported elsewhere.

As expected doped forms of polymers of 3-BAP synthesized in the presence of PSS, TMC, CSA dopants, or in buffered solutions exhibit no photoluminescence.

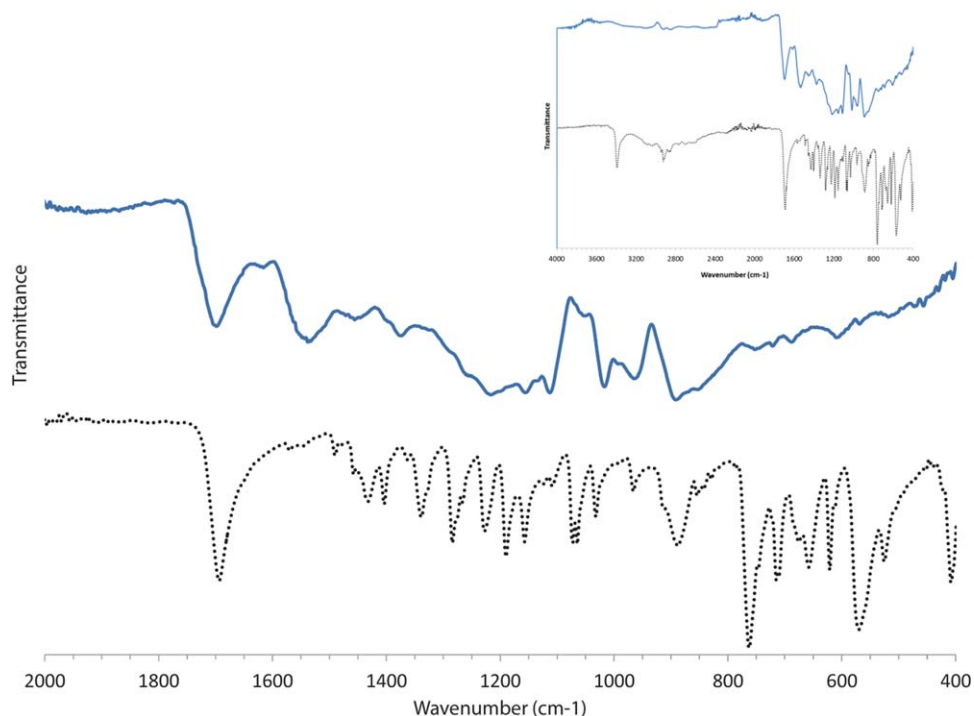
### Oligo (3BAP)—A Highly Sensitive Metal Ion Sensor

The delocalization of excited state excitons within fluorescent CPs makes them effective and sensitive sensors for the detection of environmental pollutants.<sup>38</sup> Therefore, the metal sensing properties of the 3-BAP oligomers are evaluated. Solutions containing metals salts are added to stock solutions of the oligomer and the fluorescence emission is monitored. Figure 6 shows the representative effects of the addition of a solution containing a metal salt, Co(II) in this case, to a solution of undoped oligomers in DMSO. Additional plots for all metal salts studied are provided in Supporting Information. The data shows that as the concentration of the metal salt is increased, the fluorescence emission intensity of the solution decreases linearly. The concentration of Co(II) in solution after the first addition is  $\sim 145$  parts per billion, therefore it is highly likely that the oligomer's detection limit lies significantly below this level. Similar plots



**Figure 3.** *In situ* <sup>1</sup>H NMR monitoring of initial stages of polymerization without a dopant.





**Figure 4.** FTIR-ATR of 3-BAP monomer (dotted line) and the undoped fluorescent Oligo(3-BAP) (solid line). Inset presents full spectrum of monomer and oligomer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

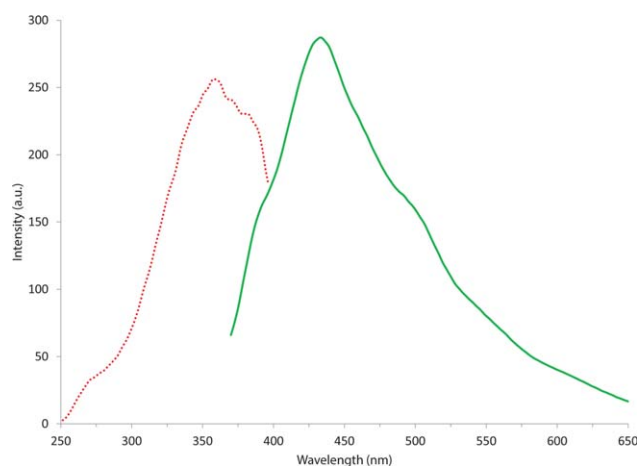
and behavior are recorded and observed for all the metal salts tested. The reduction in fluorescence is not due to a dilution effect caused by the addition of the metal salt solution. A dilution effect of less than 10% of the original fluorescence intensity is observed when the maximum addition of DMSO, containing no metal salts, is added.

The Stern-Volmer relationship is used to analyze the sensitivity of the oligomer's fluorescence to quenching by metal salts in solution. A quantitative measure of fluorescence quenching is determined using the Stern-Volmer constant,  $K_{SV}$  in eq. (1). A

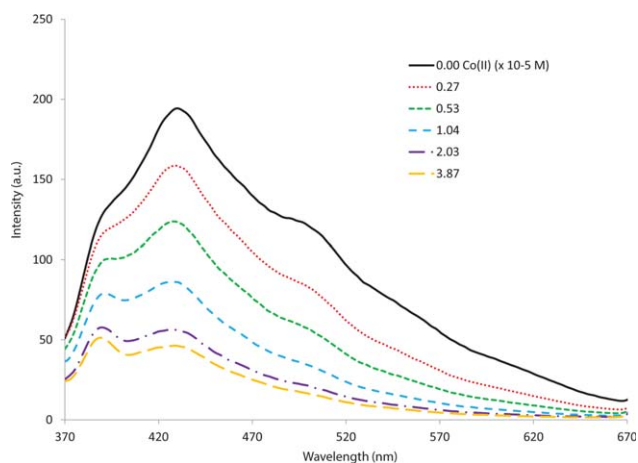
higher  $K_{SV}$  value shows an increased sensitivity towards a particular analyte.

$$(I^{\circ})/I = K_{sv} * [Q] + 1 \quad (1)$$

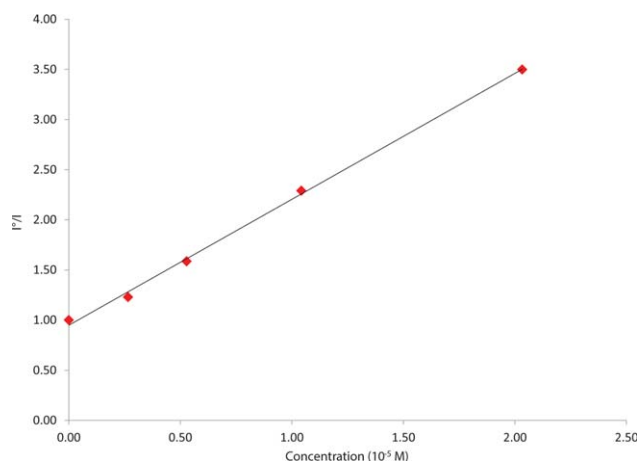
In eq. (1), Q represents the concentration of the analyte in solution, while  $I^{\circ}$  and I are the fluorescence intensities of the oligomer in the absence and in the presence of a metal salt at a given wavelength, respectively. Figure 7 presents the Stern-Volmer plot for the detection of Co(II) in DMSO. Similar plots are produced for all metal salts and can be found in Supporting Information.



**Figure 5.** Emission (solid line,  $\lambda_{ex} = 350$  nm) and excitation (dotted line,  $\lambda_{em} = 433$  nm) spectra of a 0.005 mg/mL solution of Oligo(3-BAP) in DMSO. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.** Effect of Cobalt(II) acetate tetrahydrate on emission of Oligo(3-BAP) in DMSO at 433 nm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Stern-Volmer plot for Co(II) detection by Oligo(3-BAP) in DMSO at 433 nm. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

From the slope of the Stern-Volmer plot for each analyte and using eq. (1), Stern-Volmer quenching constants are calculated. Stern-Volmer constants for all of the evaluated analytes are summarized in Table I.

The results show that the fluorescence emission of the oligomer is strongly quenched by metal salts in solution. The quenching is most sensitive in the case of Co(II) and Cu(II) salts, while Fe(II) proved to be the weakest quencher tested. Similar trends have been observed in other classes of fluorescent CPs.<sup>39</sup>

The  $K_{SV}$  values reported here demonstrate that fluorescent oligomers of 3-BAP exhibits very high sensitivity. As a comparison, Stern Volmer constants for the detection of Hg(II) using films of 1-hydroxypyrene-3,6,8-trisulfonate and polyacryloyl chloride are reported to be  $3200 M^{-1}$ .<sup>40</sup> Here we observed sensitivities to be an order of magnitude higher. It must be noted that these detection limits are unoptimized. Efforts are underway to significantly control the quality of the fluorescent oligomers to substantially lower their limit of detection.

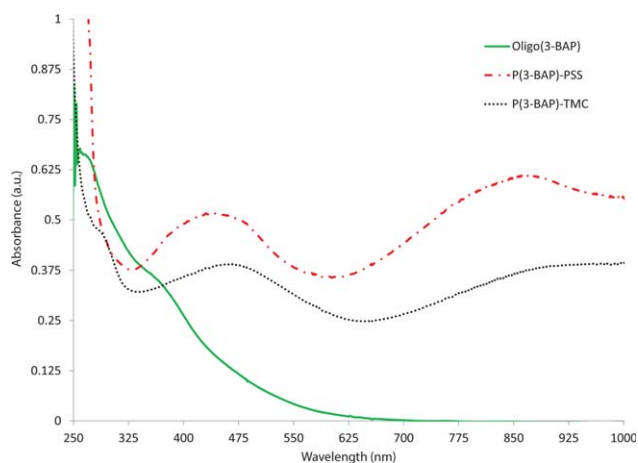
The enhanced sensitivity of detection results from the electron rich oligomer backbone and a strong binding effect caused by attraction between the carboxylic acid side chain and the metal salts. Similar polymer-side chain enhancements are observed elsewhere.<sup>41</sup> While it is unclear if either the acid side chain or the metal salts are disassociated in DMSO, functionalizing the acid group with *n*-hexylamine significantly decreases the quenching effects of Co (II) ( $K_{sv} = 31,530 M^{-1}$ ) and Cu (II) ( $K_{sv} = 19,170 M^{-1}$ ) salts (Supporting Information). This observation indicates that the enhancing attraction between the oligomers and the metal salts is likely electrostatic in nature.

**Table I.** Stern-Volmer Constants for Metal Quenching of Oligo(3-BAP) in DMSO

| Metal complex <sup>a</sup>                      | Co(II)  | Cu(II)  | Cu(II) | Hg(II) | Fe(II) |
|---|---------|---------|--------|--------|--------|
| Stern volmer constant ( $M^{-1}$ ) <sup>b</sup> | 125,000 | 111,000 | 39,100 | 34,200 | 18,700 |

<sup>a</sup> Cu(II) =  $Cu(CO_2CH_3)_2 \cdot H_2O$ , Cu(I) =  $[Cu(CH_3CN)_4]PF_6$ , Hg(II) =  $(CH_3COO)_2Hg$ , Co(II) =  $(CH_3COO)_2Co \cdot 4H_2O$ , Fe(II) =  $FeSO_4 \cdot 7H_2O$ .

<sup>b</sup> Calculated at 433 nm.



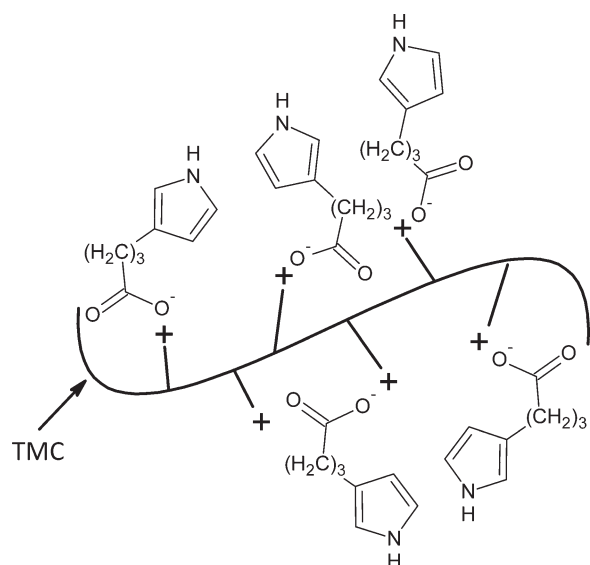
**Figure 8.** Absorption spectra of Oligo(3-BAP) (solid) and P(3-BAP) in the presence of PSS (dash-dot) or TMC (dots). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Doped Electrically Conducting Poly[4-(3-pyrrolyl)Butyric Acid]

Oxidative polymerization is also observed in buffered solutions in the presence of a small molecule dopant or a polymeric template. Reactions conducted in the presence of polymeric templates, PSS, and TMC, produced stable dispersions. Electrically conducting polymers doped with PSS or TMC are also insoluble in common organic solvents, but can be dispersed in aqueous solutions post isolation. CSA doped products are insoluble in all solvents. Polymers synthesized with PSS or TMC are electrostatically complexed with their polymeric dopants; therefore molecular weight of the products by themselves cannot be determined by gel permeation chromatography or MALDI-ToF.

A doped species with a characteristic bipolaron absorption spectrum<sup>42</sup> ( $\lambda_{max} \sim 440$  nm and greater than 800 nm) is obtained when the reaction is conducted in the presence of either PSS or the cationic template, TMC, as shown in Figure 8. While it has been well documented that polypyrroles can be doped with anionic compounds, it is rare to observe bipolaron absorption from polypyrroles synthesized in the presence a cationic template. This phenomenon has also been reported in carboxylic acid containing polyanilines synthesized in the presence of the cationic template, poly(diallyl dimethyl ammonium chloride).<sup>43</sup>

When the reaction is carried out in the presence of TMC, it is postulated that the cationic template preferentially aligns the monomer due to interactions between the anionic carboxylic acid and the cationic quaternary ammonium group of TMC. Figure 9 presents a depiction of these interactions. The actual charge balancing dopant for the oxidized conjugated backbone of polymer is likely the chloride counter ion to the quaternary



**Figure 9.** Alignment of 4-(3-Pyrrolyl)butyric acid along the cationic template, TMC.

ammonium salt of TMC or the carboxylic acid group of the adjacent 3-BAP repeat unit.

#### Electrical Conductivity of the Doped P(3-BAP) and Oligo(3-BAP)

The doped polymeric product exhibits 4-probe electrical conductivity values between  $10^{-2}$  and  $10^{-5}$  S/cm depending on the dopant. The highest conductivity ( $1.47 \times 10^{-2}$  S/cm) is obtained when the product is synthesized in a citrate buffered pH 3.5 solution in the presence of CSA. Polymers doped with PSS and TMC exhibited conductivity values of  $2.8 \times 10^{-4}$  S/cm and  $3.2 \times 10^{-3}$  S/cm, respectively. The small molecular size of CSA compared with PSS and TMC likely enables stronger doping interactions with the P(3-BAP) backbone due to less steric hindrance; thus, this increases the solid state conductivity of the final complex. Similar doping behavior has been observed previously in polypyrroles.<sup>9</sup>

The undoped fluorescent oligomer exhibits a conductivity value of  $5.2 \times 10^{-5}$  S/cm as a pressed pellet, despite showing no evidence of doping in its solution state absorption spectrum. The undoped oligomer's conductivity is likely due to self-doping in the solid state from the carboxylic acid side chain.

#### CONCLUSIONS

We present for the first time the enzymatic polymerization of a monomer, 4-(3-Pyrrolyl)butyric acid to yield a fluorescent conjugated polymer. The SBP catalyzed reaction is simple and readily tailorable for the creation of fluorescent oligomers. When the reaction is run in unbuffered DI water, with only monomer, enzyme, and dilute  $H_2O_2$ , a fluorescent oligomer is obtained. Doped, electrically conducting polymers of 3-BAP are synthesized using a similar approach, but in the presence of small molecule or polymeric dopants. When the reaction is conducted in the presence of either an anionic or cationic dopant/templates, a doped polymer with conductivity values as high as  $10^{-2}$  S/cm is obtained. MALDI-ToF and *in situ*  $^1H$  NMR results

indicate that the undoped product is a highly structurally strained oligomer, most likely coupled through the 2 and 4 positions on the pyrrole ring. The oligomer exhibits stable photoluminescent properties, a rarity for polypyrroles. When excited at 350 nm, oligomer solutions in DMSO exhibit stable emission at 433 nm. Moreover, we have demonstrated that the oligomers are excellent fluorescence sensors for the detection of metal salts with Stern-Volmer quenching constants reaching levels as high as  $125,000 M^{-1}$ .

#### ACKNOWLEDGMENTS

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