

# Molecular Engineering of Conjugated Polymers for Sensor Applications

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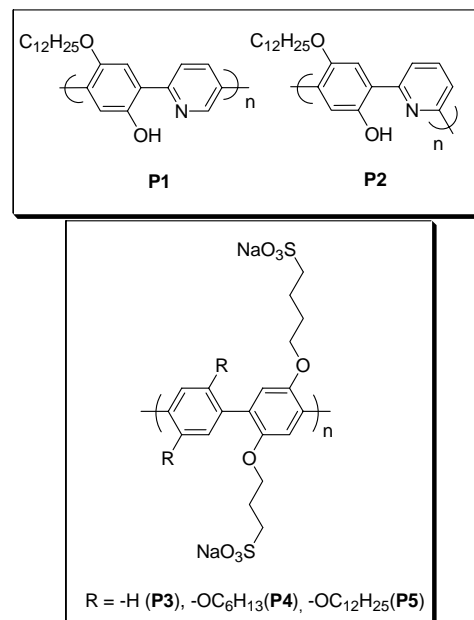
**Abstract** - In recent years, the application of fluorescent conjugated polymers for sensing chemical and biological analytes has received much attention from many researchers. A promising development in this direction was the fabrication of conducting polymer-based sensors for the detection of metal ions, small organic molecules and biomolecules. Herein, we have designed, synthesized and studied a series of copolymers containing alternate phenylene and 2,5- or 2,6-substituted pyridine rings. The basic N-atom of the pyridine ring and the adjacent -OH group from the phenyl ring provide binding sites for metal ions. Another series of water-soluble conjugated polymers with propoxy sulfonate side chains are investigated for biosensor applications. Significant quenching of the polymer fluorescence upon addition of viologen derivatives was also observed. The quenching effect on the polymer fluorescence confirmed that the newly synthesized polymers can be useful in the application of metal and biological sensors.

**Index Terms** – conjugated polymer, poly(para phenylene), fluorescence, metal ion sensor, biosensor.

## I. INTRODUCTION

Fluorescent conjugated polymers are one of the most attractive areas of research due to their various applications as light-emitting diodes,<sup>1,4</sup> laser diodes,<sup>5-7</sup> fluorescent polarizers,<sup>8</sup> chemical and biosensors,<sup>9-14</sup> electronic and photo voltaic devices.<sup>15-19</sup> Conjugated polymers are also used as sensory materials due to their high sensing properties, thermal stability and good processability. Conjugated polymers consisting hetero-donor systems such as pyridine, bipyridine, crown ethers, terpyridine, quinoline, phenothiazoline, benzimidazole and pyridine have been reported as fluorescent metal ion sensory materials.<sup>20-24</sup> These polymers are soluble only in organic solvents. For biosensor applications, the conjugated polymers were functionalized with cationic or anionic, groups depending upon the nature of biological guests. A few water-soluble conjugated polymers with anionic and cationic pendants incorporated PPV and PPP are known.<sup>25-35</sup>

Chen *et al.* proposed a novel biosensor system using the fluorescence quenching of water-soluble PPV incorporating sulfonate side groups.<sup>14</sup> They reported that the fluorescence of MBL-PPV is quenched by the electron acceptor, methyl viologen, (MV<sup>2+</sup>) with high efficiency. Such conjugated anionic polymers were reported to have high fluorescence quenching properties upon interaction with cationic species such as cytochrome-C or lysozymes, possibly based on either on dislocation of electrons through out the polymer backbone or the formation of electrostatic complexation, indicating the sensor application especially for cationic counterparts.<sup>34</sup> These sensors can be applied to chemical and biological systems as well as medical fields of toxicology, medical diagnosis, etc.<sup>12, 36</sup>



**Figure 1.** Structure of conjugated polymers for metal sensors (P1-P2) and biosensors (P3-P5)

We are interested in the synthesis and application of asymmetrically functionalized conjugated poly(para phenylenes).<sup>37-40</sup> Here, we report the synthesis of conjugated polymers consisting alternate, asymmetrically substituted phenylene and 2,5- or 2,6-substituted pyridine units (Figure 1) as metal ion sensors. In the second part, the synthesis and characterization of poly(para phenylene) polymers with sulfonatopropoxy side chains are explored.

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These are copolymers consisting of phenyl rings with disubstituted long alkyl chains and the sulfonated side chains. The polymers are water soluble due to the presence of sulfonate side chain groups. The fluorescence quenching effects of the conjugated polymers with the viologen derivatives (methyl-, ethyl- and benzyl viologen) have also been examined in detail. Preliminary results indicate that these materials are promising candidates for bio-sensor applications.

## II. EXPERIMENTAL

### A. Materials and Methods

**Instruments.** The NMR spectra were collected on a Bruker ACF 300 spectrometer, with chloroform-*d* or DMSO-*d*<sub>6</sub> as solvent and tetramethylsilane as internal standard. FT-IR spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr. UV-Vis spectra were recorded on a Shimadzu 3101 PC spectrophotometer. Fluorescence measurements were carried out on a RF-5301PC Shimadzu spectrofluorophotometer. Gel permeation chromatography (GPC) was used to obtain the molecular weight of the precursor polymers, with reference to polystyrene standards, using THF as solvent.

**Materials.** All reagents were purchased from Aldrich, Fluka or Merck and were used without further purification, unless otherwise stated. All reactions were carried out with dry, freshly distilled solvents under anhydrous conditions or in an inert atmosphere. Tetrahydrofuran was purified by distillation over sodium under nitrogen atmosphere.

### B. Synthesis

Synthetic schemes for the polymers **P1-P2** and **P3-P5** are shown in Scheme 1 and 2, respectively. 2,5-dibromo hydroquinone (**2**), 2,5-dibromo-1,4-dialkoxybenzene (**3**), 1,4-dialkoxyphenyl-2,5-bis(boronic acid) (**4**) and 1,4-dibromo-2,5-bis(3-sulfonatopropoxy) benzene sodium salt (**5**) were synthesized using the standard procedure reported in the literature.<sup>41-43</sup> The precursor polymers of **P1** and **P2** were synthesized as reported before.<sup>39-40</sup>

#### General synthesis of polymers **P1& P2**

Precursor polymer **9** (1.00 g) was dissolved in a mixture of CHCl<sub>3</sub>/THF/EtOH (100:50:30 mL) at room temperature. 10 % Pd/C (5.0 g) and three drops of Conc. HCl were added and the mixture was flushed with nitrogen gas. The flask was fitted with a hydrogen gas balloon, the mixture stirred at room temperature for 48 h, filtered through a short silica gel/celite column and the filtrate was concentrated under reduced pressure. The concentrated solution was poured into excess of methanol. The obtained precipitate was filtered and washed with methanol followed by acetone.

[**P1**]<sup>1</sup>H NMR (CDCl<sub>3</sub>/CF<sub>3</sub>COOD, δ ppm): 9.02 (b, 1H, py-H), 8.82 (b, 1H, py-H), 8.35 (b, 1H, py-H), 7.66 (b, 1H, Ar-H), 7.30 (b, 1H, Ar-H), 4.17 (b, 2H, PhOCH<sub>2</sub>CH<sub>2</sub>-),

1.91 (b, 2H, -OCH<sub>2</sub>CH<sub>2</sub>-), 1.31 (b, 18H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 0.92 (b, 3H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 190.7, 149.8, 136.8, 131.8, 128.5, 128.4, 127.8, 127.2, 71.8, 31.8, 29.6, 26.0, 22.6, 14.0, 6.6. FT-IR (KBr, cm<sup>-1</sup>): 3408, 3061, 2923, 2852, 2037, 1945, 1591, 1545, 1505, 1462, 1417, 1219, 1017, 844, 734, 696.

[**P2**]<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ ppm): 9.80 (s, 1H, py-H), 8.00 (b, 1H, py-H), 7.87 (b, 1H, py-H), 7.71 (b, 1H, Ar-H), 7.46 (s, 1H, Ar-H), 4.14 (b, 2H, PhOCH<sub>2</sub>CH<sub>2</sub>-), 1.78 (b, 2H, -OCH<sub>2</sub>CH<sub>2</sub>-), 1.26 (b, 18H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 0.86 (b, 1H, -CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 191.0, 190.0, 159.5, 134.5, 128.4, 128.3, 127.4, 125.4, 63.2, 31.7, 29.5, 26.1, 22.5, 13.9, 6.9. FT-IR (KBr, cm<sup>-1</sup>): 3437, 3059, 2923, 2852, 1567, 1505, 1451, 1375, 1198, 1020, 812, 733, 695.

#### Synthesis of sulfonated polymers (**P3-P5**)

Dialkoxy boronic acid [**4**] (1.0 g, 2.73 mmol) and disulfonated compound [**5**] (0.76 g, 2.73 mmol) were mixed in 35 mL of DMF. 50 mL of Na<sub>2</sub>CO<sub>3</sub> solution (2M) was added to the mixture followed by degassing for about 8 hrs. Once the catalyst [tetrakis (triphenylphosphino) palladium, 2 mol% with respect to monomers] was added, the mixture was heated up to 85 °C for 72 hrs and concentrated under pressure. The resultant solid was dissolved in H<sub>2</sub>O, dialyzed for 48 hrs in 3500 g mol<sup>-1</sup> cutoff membrane and vacuum dried to get a tan solid with yield of 60 %.

[**P3**]<sup>1</sup>H NMR (DMSO, δ ppm): 7.01 (b), 3.91 (b), 3.09 (b), 2.18 (b). <sup>13</sup>C NMR (DMSO, δ ppm): 149.8, 137.0, 130.0, 118.1, 69.0, 48.2, 25.1. FT-IR (KBr, cm<sup>-1</sup>): 3032, 2943, 2864, 2357, 1642, 1518, 1210, 1051, 825, 766, 607. Mn = 2459, Mw = 3501, PDI = 1.01.

[**P4**]<sup>1</sup>H NMR (DMSO, δ ppm): 7.06 (b), 3.93 (b), 2.87 (b), 2.04 (b), 1.57 (b), 1.16 (b), 0.87 (b). <sup>13</sup>C NMR (DMSO, δ ppm): 147.5, 121.4, 106.8, 68.6, 48.0, 30.9, 28.9, 25.1, 22.0, 13, 8. FT-IR (KBr, cm<sup>-1</sup>): 2932, 2867, 2352, 1630, 1470, 1388, 1210, 1044, 796, 730, 612. Mn = 4764, Mw = 4793, PDI = 1.01.

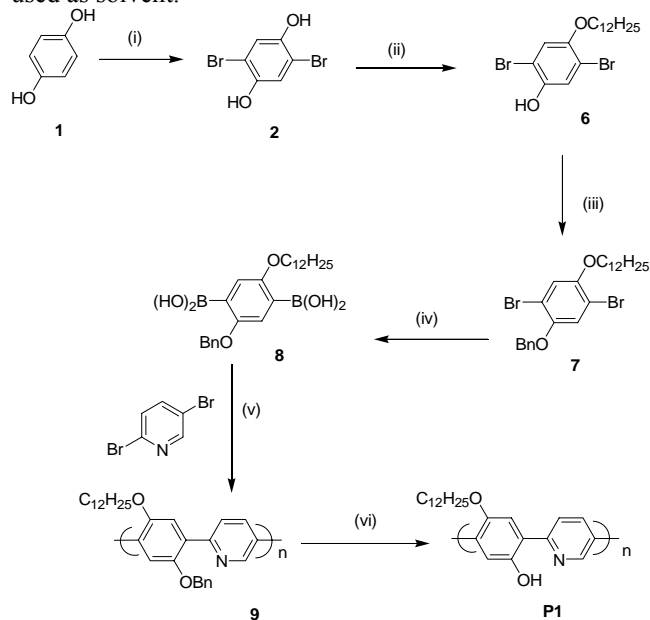
[**P5**]<sup>1</sup>H NMR (DMSO, δ ppm): 7.04 (b), 3.92 (b), 2.81 (b), 1.97 (b), 1.55 (b), 1.14 (b) 0.80 (b). <sup>13</sup>C NMR (DMSO, δ ppm): 149.5, 118.2, 110.5, 68.8, 47.8, 30.6, 29.0, 25.5, 22.5, 14.0. FT-IR (KBr, cm<sup>-1</sup>): 2932, 2878, 2323, 1624, 1494, 1192, 1054, 802, 623. Mn = 7227, Mw = 7720, PDI = 1.07.

## III. RESULTS AND DISCUSSION

### Synthesis of polymers

The general synthetic route for the monomers and polymers, **P1-P2** and **P3-P5**, are outlined in Schemes 1 and 2, respectively. The monomer 1,4-dialkoxyphenyl-2,5-bis(boronic acid) (**4**) was synthesized from hydroquinone using reported procedures.<sup>42</sup> 2,5-Dibromohydroquinone (**2**) was obtained by bromination of hydroquinone with bromine in acetic acid.<sup>41</sup> Alkylation of **2** with alkylbromide in presence of NaOH/EtOH, at 60 °C gave compound **3**, which was reacted with *n*-butyl lithium followed by quenching with triisopropylborate and hydrolyzed with

hydrochloric acid to afford bis(boronic acid) **4**. All polymerizations were done using Suzuki polycondensation reactions.<sup>42-43</sup> In the case of **P1 - P2**, polymerizations were carried out in a mixture (2:3 v/v) of toluene and K<sub>2</sub>CO<sub>3</sub> solution (2M) containing 3.0 mol% Pd(PPh<sub>3</sub>)<sub>4</sub> with vigorous stirring at 85-90 °C for 72 hrs in nitrogen atmosphere and purified. In the case of **P3-P5**, DMF was used as solvent.

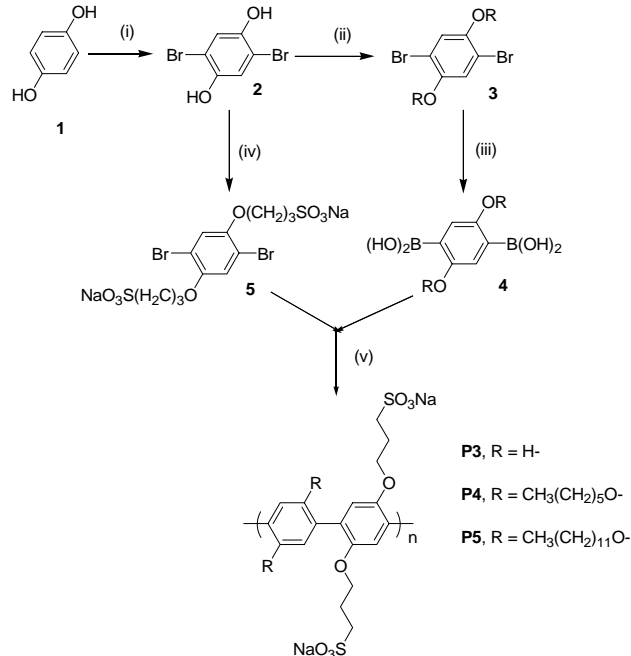


**Scheme 1:** Synthesis of polymer **P1**: (i) Br<sub>2</sub>/AcOH, 80 %; (ii) NaOH in abs. EtOH, CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>Br, 45-50°C, 10h, 65 %; (iii) K<sub>2</sub>CO<sub>3</sub> in abs. EtOH, C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Br, 50°C, 10h, 90 %; (iv) 1.6 M soln of n-BuLi in hexane, THF at -78 °C, triisopropylborate, stirred at RT for 10 hrs, 70 %; (v) 2M K<sub>2</sub>CO<sub>3</sub> solution, toluene, 3.0 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>, reflux for 3 d, (vi) H<sub>2</sub>, 10 % Pd/C, CHCl<sub>3</sub>/EtOH/THF.

**Characterization of Polymers.** All polymers [**P1-P5**] were characterized using <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT-IR, GPC, TGA and X-ray diffraction studies. The assignments of the <sup>1</sup>H and <sup>13</sup>C NMR peaks are given in the experimental section. The molecular weights of the water-soluble conjugated polymers are difficult to evaluate due to their aggregation behavior and polyelectrolyte nature.<sup>25</sup> A few research groups<sup>29,43,44</sup> reported that the GPC results using polystyrene standards may not be reliable due to the higher rigid nature of the PPP backbones and the presence of polar functional groups. All polymers gave broad signals in <sup>1</sup>H-NMR spectra. For the polymer **P1**, the pyridine protons are observed at 8.3 - 9.0 ppm and phenylene protons are observed at 7.3 - 7.6 ppm. The peaks at 4.17 and 1.9 - 0.9 ppm are due to the PhOCH<sub>2</sub>- protons and other aliphatic chain protons, respectively.

For the polymer **P4**, the peaks at 7.06 ppm for phenylene protons, 3.93, 2.87 and 2.04 ppm for the -CH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub><sup>-</sup> groups, and 1.57, 1.16 and 0.87 ppm for the dialkyl chain groups were observed. In <sup>13</sup>C-NMR, there were three distinct regions 147.5, 121.4 and 106.8 ppm for phenylene carbons, 68.6, 48.0 and 25.1 ppm for propoxy sulfonate

carbons, and 30.9, 28.9, 22.0 and 13.8 ppm for the long alkyl chain groups. Similar patterns of NMR spectra were observed for the other polymers also. In FT-IR, the symmetric S=O stretching of the sulfonate groups for the polymers **P3, P4** and **P5** are observed at 1051, 1044 and 1048 cm<sup>-1</sup>, and the asymmetric S=O stretching of the sulfonate groups for the polymers are observed at 1210, 1210 and 1163 cm<sup>-1</sup>. The aromatic C=C and C-H stretching are observed at 1630 - 1640 and 3032 - 3050 cm<sup>-1</sup>.



**Scheme 2:** Synthesis of polymers **P3-P5**: (i) Br<sub>2</sub>/AcOH, 80 %; (ii) NaOH in abs. EtOH, RBr, 60° C, 10h, 65 %; (iii) 1.6 M soln of n-BuLi in hexane, THF at -78 °C, triisopropylborate, stirred at RT for 10h, 60 %; (iv) NaOH, EtOH, 1,3-propane sultone, 24h (v) 2M Na<sub>2</sub>CO<sub>3</sub> solution, DMF, 3.0 mol% Pd(PPh<sub>3</sub>)<sub>4</sub>, reflux for 3 days.

## Sensing Applications

### (a) Chemical Sensor

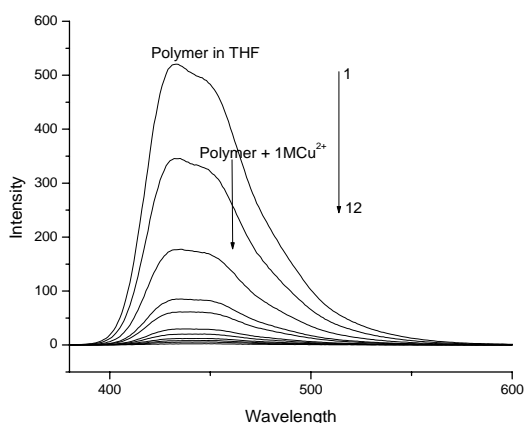
By considering the good complexation ability of the pyridine and adjacent phenolic hydroxyl group, the ionochromic effects of the polymers **P1-P2** were studied using alkali, alkaline earth, transition and rare-earth metal ions. The ion responsive optical properties of the polymers were monitored by the addition of methanolic solution of the metal salts into a THF solution of the polymers. The apparent metal ionochromic effect of the polymers is the rapid color change of polymer solutions. The colors vary from originally colorless or yellow to pink, green, purple, reddish brown, etc., depending on the metal ions and polymers. The differences in the absorption maxima ( $\Delta\lambda_{\max}$ ) of the polymers upon addition of metal ions are tabulated in Table 1.

The red shift in the  $\lambda_{\max}$  was attributed to the conjugation enhancement along the polymer backbone induced by the coordination of metal ions with the pyridine nitrogen and phenolic group. For different metal ions, the differences in the absorption maximum reflected the different

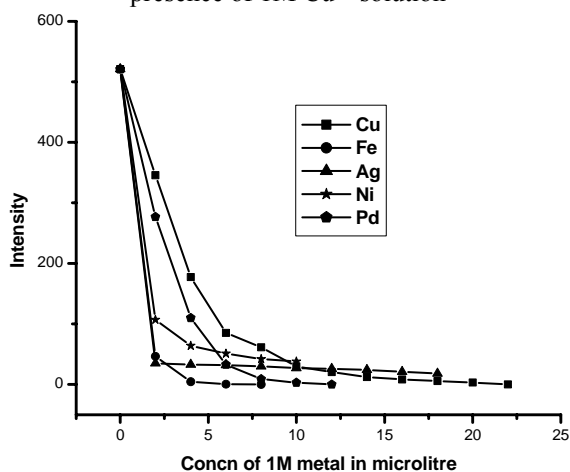
coordination ability of metal ions and the stronger coordination induced a larger spectral red shift.

**Table 1.** Absorption responses of P1-P2 upon addition of metal ions.

$(\lambda_{\max})$ Ion free		Polymer P1	Polymer P2
		383	360
$(\Delta\lambda_{\max})$	$\text{Cu}^{2+}$	44	49
	$\text{Fe}^{3+}$	144	114
	$\text{Co}^{2+}$	15	4
	$\text{Ni}^{2+}$	6	-
	$\text{Pd}^{2+}$	18	-
	$\text{Mn}^{2+}$	5	-
	$\text{Zn}^{2+}$	3	-
	$\text{Ag}^+$	11	4
	$\text{Mg}^{2+}$	3	-
	$\text{Pr}^{3+}$	8	-



**Figure 2.** Changes in the emission spectra of P1 in presence of 1M  $\text{Cu}^{2+}$  solution



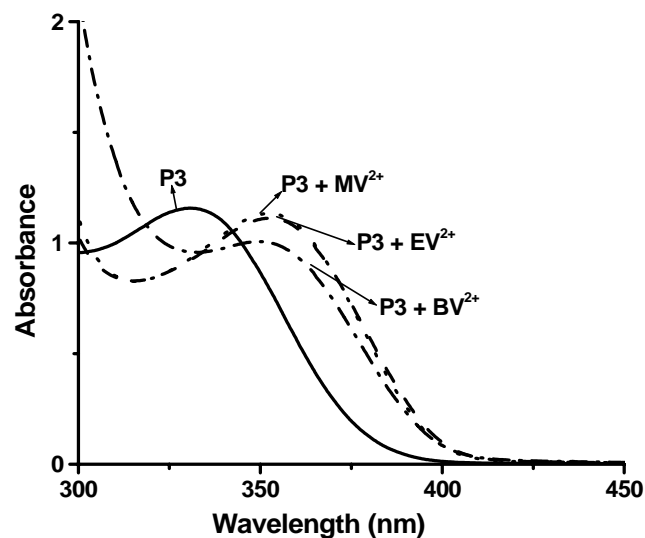
**Figure 3.** Titration curves of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  to the polymer P1 in THF solution.

The optical properties of polymers **P1-P2** are influenced by the addition of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  metal ions. In addition to  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$ , polymers **P1-P2** showed ionochromic effects in the presence of  $\text{Co}^{2+}$  and  $\text{Ag}^+$  metals (Table 1). Polymer **P1** seems better at sensing the variety of metal ions studied,

which may be due to the 1,4-linkage of all aromatic rings on the polymer backbone, and the adjacent position of pyridine nitrogen and phenolic group for the metal complexation. Addition of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  solutions into the **P1** solution resulted in a red-shift of 44 and 144 nm, respectively. Figure 2 depicts the fluorescence spectra of the polymer **P1** in THF upon adding different amounts of  $\text{Cu}^{2+}$ . The corresponding titration curve is shown in Figure 3 together with additional metal ions for comparison.

### (b) Biosensing Applications

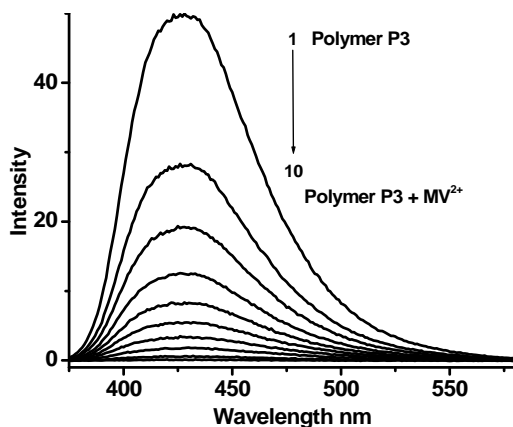
The aggregation of water-soluble polymers is enhanced by the addition of ionic quenchers.<sup>34</sup> The absorption spectra for the polymers **P3-P5** in presence of viologen derivatives ( $\text{MV}^{2+}$ ,  $\text{EV}^{2+}$ ,  $\text{BV}^{2+}$ ) were investigated in water. The UV-Vis absorption of the polymer **P3** with and without methyl viologen is shown in Figure 4. For **P3**, a red shift of 21 nm in the  $\lambda_{\max}$ , in presence of viologen derivatives (methyl, ethyl and benzyl), was observed. In addition to the shift in the absorption, a new absorption peak around 258 nm was also seen in spectra. This band is believed to be the new absorption due to formation of polymer-viologen complexes. The intensity of this peak increases as the concentration of viologen increases. In addition, a decrease in intensity of the absorption peak at 331 nm was observed with increase in concentration of viologen derivatives. Though the shift in the absorption for the three viologen derivatives is same, the decrease in the intensities of absorption peak follows the order, methyl  $\approx$  ethyl > benzyl viologen. Such observations were also reported for MBL-PPV polymer before.<sup>34</sup> Similar types of differences in the wavelength on the addition of the viologen derivatives for polymers **P1-P3** (either red or blue shift) were also observed.



**Figure 4.** Absorption spectrum of the polymer **P3** on the addition of viologen derivatives

Since the fluorescence of the polymers can be effectively quenched by the addition of cationically charged systems, water-soluble conjugated polymers with anionic sulfonate side chain groups are good candidates for the biosensor

applications.<sup>10,11,14,32-35</sup> The quenching effects on polymer fluorescence due to the addition of viologen derivatives have been investigated in detail. In general, there are two types of quenching, one is static quenching through the formation of a complex and the other is dynamic quenching due to the random collisions between the emitter and the quencher. Both quenching mechanisms involve electron transfer from the emitter to the quencher and each can be quantitatively described by the Stern-Volmer studies.<sup>45</sup> The Stern-Volmer equation is given by the relation,  $I_0/I = 1 + K_{SV} [\text{Quencher}]$ , where  $I_0$  is the intensity of the fluorescence from the polymer solution in the absence of quencher and  $I$  is the intensity in presence of the quencher.  $K_{SV}$  is the Stern-Volmer constant which provides the quantitative measure of the quenching.



**Figure 5.** Changes in the emission spectra of **P3** in water at different concentrations of methyl viologen (1) 0  $\mu\text{M}$ , (2) 0.1  $\mu\text{M}$ , (3) 0.2  $\mu\text{M}$ , (4) 0.3  $\mu\text{M}$ , (5) 0.5  $\mu\text{M}$ , (6) 0.7  $\mu\text{M}$ , (7) 1.0  $\mu\text{M}$ , (8) 1.5  $\mu\text{M}$ , (9) 2.5  $\mu\text{M}$ , (10) 4.0  $\mu\text{M}$ . Concentration of **P3** was  $1.45 \times 10^{-5}$  M.

The fluorescence spectrum of the polymer **P3** is quenched by the addition of the methyl viologen. The quenching effect increased with increase in concentration of the methyl viologen as shown in Figure 5 and complete quenching was observed on the addition of 4.0  $\mu\text{M}$  solution of methyl viologen. In very dilute conditions, the quenching efficiency increases and  $I_0/I$  Vs (Quencher) gives a linear plot.<sup>45</sup> We have studied the quenching behavior of our polymers with  $\text{MV}^{2+}$ ,  $\text{EV}^{2+}$  and  $\text{BV}^{2+}$ . Under low concentrations (lower than 1.0  $\mu\text{M}$ ) of viologen derivatives, all the polymers gave a linear relationship of  $I_0/I$  vs. [Quencher]. The Stern-Volmer constant  $K_{SV}$  for the polymers are tabulated in the Table 2. The Stern-Volmer plots for polymer **P3** upon addition of  $\text{MV}^{2+}$ ,  $\text{EV}^{2+}$  and  $\text{BV}^{2+}$  are shown in Figure 6.

Among the polymers **P3-P5**, the polymer **P3**, without dialkyl chain gave the highest Stern-Volmer constant for the quenching effects addition of viologen derivatives. The highest  $K_{SV}$  value obtained in our systems was on addition of  $\text{BV}$  into the polymer **P3**, which is  $2.0 \times 10^7$ . As there are no dialkyl chains, the interaction of the viologen

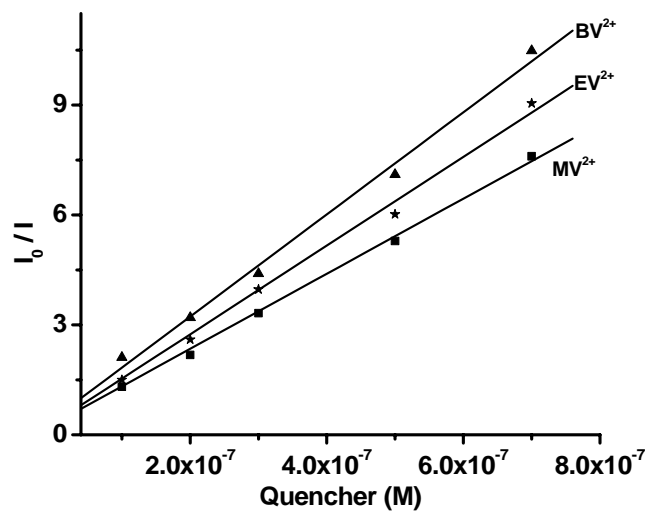
derivatives with the polymer may be higher, which may result in efficient quenching of the fluorescence. This is reflected in the case of **P4** and **P5** as well.

Quenching efficiencies also increase as the size of the side chain increases. Among the three viologen derivatives, the benzyl viologen quenches with significantly higher  $K_{SV}$  than ethyl viologen which is higher than methyl viologen. Such variation due to the carbon chain lengths in the viologen derivatives have been reported before for PPV-related polymer.<sup>34</sup> The reason for such observations may be due to (i) elongation of the side chain which increases the collision of the polymer and viologen, (ii) reorganization energy and (iii) the hydrophobicity of the viologen derivatives, which increases with the chain length.<sup>34</sup>

**Table 2.** Stern-Volmer constants for the polymers upon addition of the quencher.

Polymer	Quenchers		
	MV	EV	BV
<b>P3</b>	$9.0 \times 10^6$	$1.0 \times 10^7$	$2.0 \times 10^7$
<b>P4</b>	$5.1 \times 10^5$	$6.5 \times 10^5$	$2.0 \times 10^6$
<b>P5</b>	$4.7 \times 10^5$	$6.2 \times 10^5$	$8.1 \times 10^5$

MV = Methyl viologen, EV = Ethyl viologen, BV = Benzyl viologen.



**Figure 6.** Stern-Volmer plots of the polymer **P3** ( $< 1 \mu\text{M}$ ) quenched by the viologen derivatives: Methyl viologen,  $\text{MV}^{2+}$  (square), Ethyl viologen,  $\text{EV}^{2+}$  (star), Benzyl viologen,  $\text{BV}^{2+}$  (triangle).

#### IV. CONCLUSIONS

A pair of conjugated poly(para phenylene)s (**P1-P2**) with pyridine units were synthesized and use of these conjugated polymers for metal sensor applications was explored. A series of water-soluble poly(para phenylenes) (**P3-P5**) with propoxy sulfonate side chains were synthesized and characterized. Due to the presence of the propoxy sulfonate side chains in the polymers, all the conjugated polymers are soluble in water. Among the polymers, the polymer **P3**, with no alkyl chain groups, gave higher/significant quenching efficiencies with the

high value of Stern-Volmer constant by the addition of viologen derivatives. Under dilute conditions, linear Stern-Volmer plots are obtained for all the polymers on the addition of the quencher. At higher concentrations, there is superlinear quenching. The highest K<sub>sv</sub> of 2.0 × 10<sup>7</sup> was obtained for the polymer **P3** among all the polymers, upon addition benzyl viologen. The quenching efficiencies increase with the increase in the side chain of the viologen derivatives. The high fluorescence quenching efficiencies of these polymers indicate that they may have better applications as biosensors.

#### ACKNOWLEDGMENTS

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