

Synthesis, Optical properties and Applications of Water Soluble Conjugated PPPs for Biosensors

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Abstract—In recent years, application of fluorescent conjugated polymers to sense chemical and biological analytes has received much attention for many researchers. Water soluble conjugated polymers are interested towards the applications in bio-sensory materials as the biological media is in aqueous. In this present contribution, we will describe the syntheses and characterization of a series of water soluble conjugated polymers with sulfonate side chains. Such anionic conjugated polymers are designed by knowing the cationic biologically important compounds such as cytochrome-c and lysozyme. These polymers are having the long alkyl and sulfonate side chain groups in symmetric fashion. The polymers are soluble in water and showed strong blue emission. Significant quenching of the polymer fluorescence upon addition of viologen derivatives or cytochrome - C was also observed. The quenching effect on the polymer fluorescence confirmed that the newly synthesized polymers can be useful in the application of biological and chemical sensors.

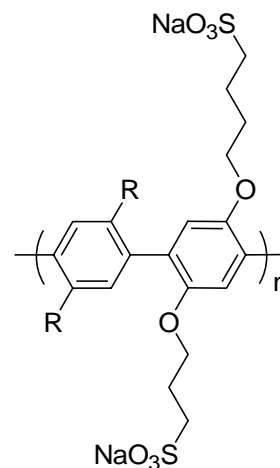
Index Terms—conjugated polymer, biosensor, fluorescence, metal ion sensor.

I. INTRODUCTION

Fluorescent conjugated polymers is one of the most attractive area of research field for a variety of applications such as light-emitting diodes,¹⁻⁴ laser diodes,⁵⁻⁷ fluorescent polarizers,⁸ chemical and biosensors,⁹⁻¹⁴ electronic and photo voltaic devices.¹⁵⁻¹⁹ Conjugated polymers are having much interest as sensory materials due to their high sensing properties, thermal stability and good processability. Conjugated polymers consisting hetero-donor systems such as bipyridine, crown ethers, terpyridine, quinoline, phenothiazoline, benzimidazole and pyridine have been reported as fluorescent and metal ion sensory materials.²⁰⁻²⁴ These polymers are soluble only in organic solvents. But for the biosensor applications, the derived polymers should be soluble in water and hence the conjugated polymers have been functionalized in the pendants as cationic or anionic, depending upon the biological guest. Few water

soluble conjugated polymers with anionic and cationic pendants incorporated in PPV and PPP are known.²⁵⁻³¹ The conjugated polymers of PPV with the ionic side chain groups have been reported for the biosensor applications.^{14,32-35}

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



R = -H, -OC₆H₁₃, -OC₁₂H₂₅, -OCH₂C₆H₅

Figure 1. Structure of Target Polymers

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We are interested in the synthesis and applications of amphiphilic conjugated poly(para phenylenes). In this work, we report the syntheses and characterization of poly (para phenylene) polymers with sulfonatopropoxy side chains. They are copolymers consisting of phenyl rings with disubstituted long alkyl chains and the sulfonated side

chains. The polymers were water soluble due to the presence of sulfonate side chain groups in the polymer backbone. The optical and thermal properties of these water soluble PPPs were characterized. The fluorescence quenching effects of the conjugated polymers with the metal cations, viologen derivatives (methyl-, ethyl- and benzyl viologen) and cytochrome-C have also been examined in detail. Preliminary results indicate that these materials offer promising candidates in bio-sensor application.

II. EXPERIMENTAL

A. Materials and Methods

Instruments. The NMR spectra were collected on a Bruker ACF 300 spectrometer with chloroform-*d* or methanol-*d*₃ 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. Thermogravimetric analyses were done using TA instruments SDT 2960 with a heating rate of 10° C/min under a nitrogen atmosphere. Gel permeation chromatography (GPC) was used to obtain the molecular weight of the precursor polymers with reference to polystyrene standards using THF as solvent. X-ray powder patterns were obtained using a D5005 Siemens X-ray diffractometer with Cu-K α (1.54 Å) radiation (40 kV, 40 mA). Samples were mounted on a sample holder and scanned with a step size of $2\theta = 0.01^\circ$ between $2\theta = 2^\circ$ to 40° .

Materials. All reagents were purchased from Aldrich, Fluka and/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 from sodium in the presence of benzophenone under a nitrogen atmosphere.

B. Synthesis

Synthetic scheme for the monomers and polymers **P0-P3** are shown in Scheme 1. Polymer **P0** is synthesized as reported before.²⁵ 2,5-dibromo hydroquinone (**2**), 2,5-dibromo-1,4-dialkoxybenzene (**3**), 1,4-dialkoxyphenyl-2,5-bis(boronic acid) (**4**), 1,4-dibromo-2,5-bis(3-sulfonatopropoxy) benzene sodium salt (**5**) were synthesized using the standard procedure reported in the literature.³⁷⁻³⁹

Dialkoxy boronic acid [**4**] (1.0 g, 2.73 mmol), disulfonated compound [**5**] (0.76 g, 2.73 mmol) were mixed in 35 mL of DMF. A 50 mL of Na₂CO₃ 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, concentrated under pressure, the resultant solid was dissolved in H₂O, dialyzed for 48 hrs in 3500 g mol⁻¹ cutoff membrane, vacuum dried to get a tan solid with an yield of 60 %.

[P0] ¹H NMR (DMSO, δ ppm): 7.01 (b), 3.91 (b), 3.09 (b), 2.18 (b). ¹³C NMR (DMSO, δ ppm): 149.8, 137.0, 130.0, 118.1, 69.0, 48.2, 25.1. FT-IR (KBr, cm⁻¹): 3032, 2943, 2864, 2357, 1642, 1518, 1210, 1051, 825, 766, 607. Mn = 2459, Mw = 3501, PDI = 1.01.

[P1] ¹H 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). ¹³C 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⁻¹): 2932, 2867, 2352, 1630, 1470, 1388, 1210, 1044, 796, 730, 612. Mn = 4764, Mw = 4793, PDI = 1.01.

[P2] ¹H 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). ¹³C 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⁻¹): 2932, 2878, 2323, 1624, 1494, 1192, 1054, 802, 623. Mn = 7227, Mw = 7720, PDI = 1.07.

[P3] ¹H NMR (DMSO, δ ppm): 7.23 (b), 7.06 (b), 4.97 (b), 3.92 (b), 2.51 (b), 1.97 (b). ¹³C NMR (DMSO, δ ppm): 147.1, 128.1, 119.2, 113.2, 68.8, 48.4, 26.9. FT-IR (KBr, cm⁻¹): 3068, 2920, 2855, 2364, 1635, 1482, 1441, 1163, 1048, 789, 742, 689. Mn = 6545, Mw = 7100, PDI = 1.08.

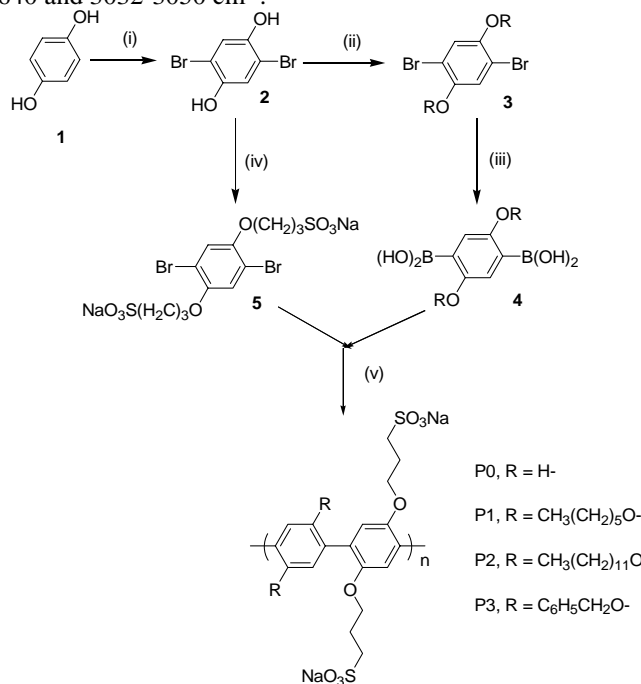
III. RESULTS AND DISCUSSION

Synthesis of polymers

The general synthetic route towards the monomers and polymers **P0-P3** are outlined in Scheme 1. The monomer 1,4-dialkoxyphenyl-2,5-bis(boronic acid) (**4**) was synthesized from hydroquinone using reported procedure.³⁸ 2,5-Dibromohydroquinone (**2**) was obtained via bromination of hydroquinone with bromine in acetic acid.³⁷ 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.³⁹⁻⁴⁰ Polymerizations were carried out in a mixture (2:3 v/v) of DMF and Na₂CO₃ solution (2M) containing 3.0 mol % Pd(PPh₃)₄ under vigorous stirring at 85-90 °C for 72 hrs in nitrogen atmosphere and purified.

Characterization of Polymers. All polymers [**P0-P3**] were characterized using ¹H-NMR, ¹³C-NMR, FT-IR, GPC, TGA and X-ray diffraction studies. The assignments of the ¹H and ¹³C 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.²⁵ A few research groups^{29,40,41} reported that the GPC results using polystyrene standards may not be reliable due to the higher

rigidity nature of the PPP backbones and the presence of polar functional groups. All the polymers gave broad signals in $^1\text{H-NMR}$ spectra. For the polymer **P1**, the peaks at 7.06 ppm for phenylene protons, 3.93, 2.87, 2.04 ppm for the $-\text{CH}_2\text{CH}_2\text{SO}_3^-$ groups and 1.57, 1.16, 0.87 ppm for the dialkyl chain groups were observed. In $^{13}\text{C-NMR}$, 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. In FT-IR, the symmetric S=O stretching of the sulfonate groups for the polymers **P0**, **P1**, **P2** and **P3** are observed at 1051, 1044, 1054 and 1048 cm^{-1} , and the asymmetric S=O stretching of the sulfonate groups for the polymers were observed at 1210, 1210, 1192, and 1163 cm^{-1} . The aromatic C=C and C-H stretching are observed at 1630-1640 and 3032-3050 cm^{-1} .



Scheme 1: Scheme 1: Synthesis of polymers **P0-P3**: (i) Br_2/AcOH , 80 %; (ii) NaOH in abs. EtOH , RBr , 45-50 °C, 10 h, 65 %; (iii) 1.6 M soln of $n\text{-BuLi}$ in hexane, THF at -78 °C, tri-isopropylborate, stirred at RT for 10 h, 60 %; (iv) NaOH , EtOH , 1,3-Propane sultone, 24 h (v) 2M Na_2CO_3 solution, DMF, 3.0 mol % $\text{Pd}(\text{PPh}_3)_4$, reflux for 3 days:

Thermal Properties

The thermal properties of the polymers were investigated by thermo gravimetric analyses at a heating rate of 10 °C/min under nitrogen atmosphere. The TGA traces of the polymers **P0-P3** are shown in Figure 2. Polymers **P1-P3** showed good thermal stability and the onset degradation temperatures were in the range of 250 – 271 °C. This decomposition corresponds to the degradation of the dialkyl groups on the polymer backbone. This is clear with the decomposition temperature of the polymer **P0**. Since, there are no alkyl chains on **P0**, only one decomposition

temperature at 400 °C is observed. Second onset temperatures at 400 – 500 °C correspond to the decomposition of the polymer backbone. Thus, two step degradations are observed for polymers **P1-P3**.

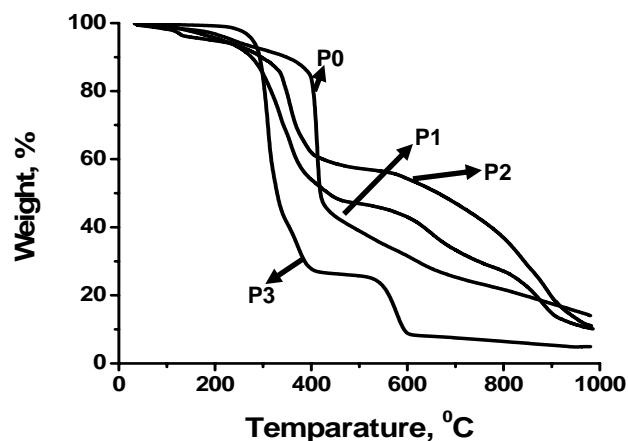


Figure 2. TGA traces of the polymers, **P0-P3**

Optical properties

(a) Absorption and Emission Spectroscopy

The optical and emission properties of the polymers **P0-P3** in water are summarized in Table 1. The absorption spectra of the polymers were shown in Figure 3a. The optical properties of the polymers in water solution are dependant on the side chains of the polymers. The absorption spectra of polymers showed maxima (λ_{max}) located in the range of 296 – 335 nm, indicating that the differences in the side chain contribute much to the overall planarization of the polymer backbone due to the longer conjugation.

Table 1. Absorption and emission wavelength for the polymers

Polymer	λ_{max} (nm)	ϵ_{max}	Band gap (eV)	λ_{emi} (nm)
P0	331	7.93×10^4	3.74	431
P1	305	1.05×10^5	4.06	398
P2	296	1.81×10^5	4.18	361
P3	299	1.95×10^5	4.14	395

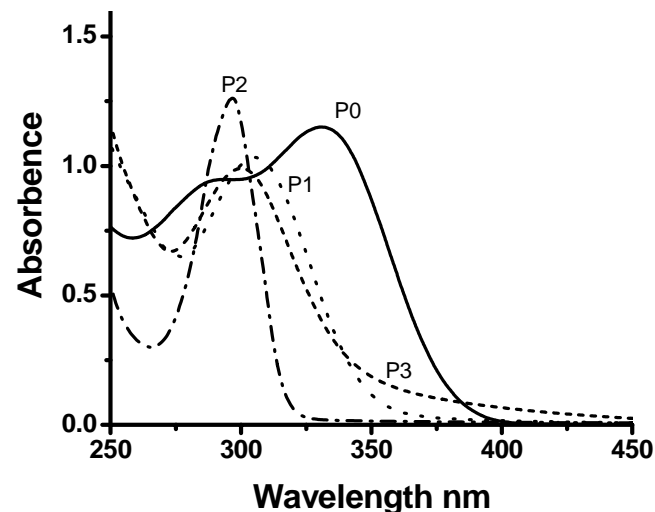


Figure 3a. UV-vis absorption for the polymers, **P0**, **P1**, **P2** and **P3**

There is a progressive hypsochromic shift in the UV-Vis absorption maximum from the polymer **P0**, the polymer without side chain to the **P3**, polymer with the longest alkyl side chain. The λ_{\max} for **P0**, **P1**, **P2** and **P3** are 331, 305, 296 and 299 nm, respectively. In water, all the polymers are highly fluorescent. The emission maxima of these polymers also follow the similar trend to that of the absorption wavelength. The λ_{emi} maxima for the polymers **P0**, **P1**, **P2** and **P3** are 431, 398, 361 and 395 nm. The fluorescence spectra for the polymers **P0-P3** are shown in Figure 3b.

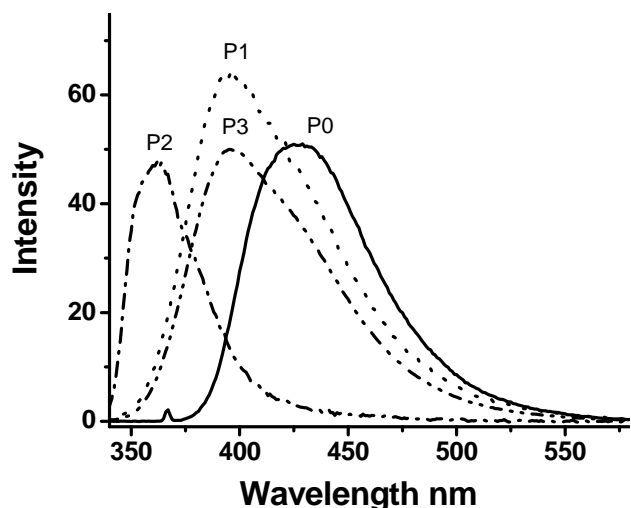


Figure 3b. Fluorescence spectra for the polymers **P0**, **P1**, **P2** and **P3**

Sensing Properties

The aggregation of water soluble polymers is enhanced by the addition of the ionic quenchers.³⁴ The absorption spectra for the polymers **P0-P3** in presence of viologen derivatives (MV^{2+} , EV^{2+} , BV^{2+}) are investigated in water. The UV-Vis absorption of the polymer **P0** with and without methyl viologen is shown in Figure 4. For **P0**, a red shift of 21 nm in the λ_{\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 that 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, were 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 increases in the order, methyl \cong ethyl > benzyl viologen. Such observation was also observed for MBL-PPV polymer before.³⁴

The decrease in the absorption by the addition of the viologen derivatives confirmed the aggregation of the water soluble polymers. Similar types of the difference in the wavelength by the addition of the viologen derivatives

for other polymers **P1-P3** (either red or blue shift) are also observed.

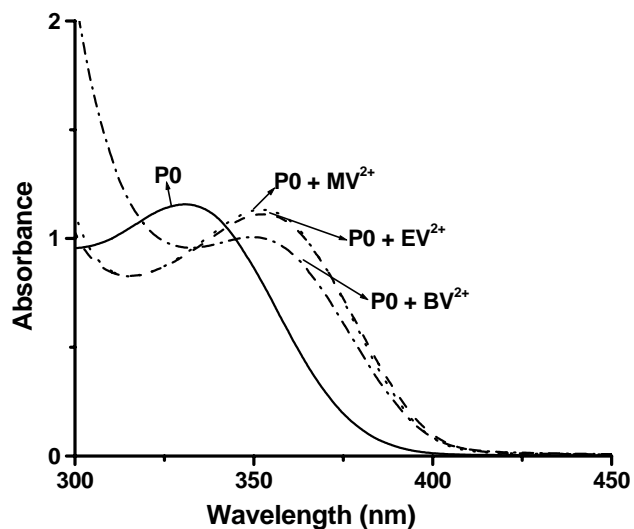
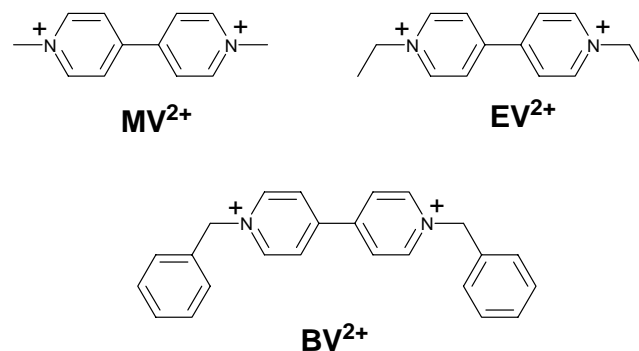


Figure 4. Absorption spectrum of the polymer **P0** by the addition of viologen derivatives

In addition to the viologen derivatives, the change in absorption by the addition of the biologically important cytochrome-C (Cyt C) has also been monitored. The high-efficiency fluorescence quenching of conjugated polymers by the Cyt C is reported by Heeger *et al.* by using the polymer MBL-PPV.³² Since the polymers, **P0-P3** are anionic in nature, the cationic poly electrolyte Cyt C is expected to quench the polymer fluorescence and the absorption. Similar to the viologen derivatives, the difference in absorption of polymer **P0** by the addition of the Cyt C is also 21 nm. The quenching effect by the addition of the Cyt C into the polymer solution is discussed in detail at a later section.

Since the fluorescence of the polymers can be effectively quenched by the addition of cationically charged system, the water soluble conjugated polymers with the anionic sulfonate side chain groups are good candidates for the biosensor applications.^{10,11,14,32-35} The quenching effects of the polymer fluorescence by the addition of viologen derivatives and the cytochrome-c 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 the dynamic quenching due to the random collisions between the emitter and the quencher. In both quenching mechanisms, the electron transfer is involved from the emitter to the quencher and each can be quantitatively described by the Stern-Volmer studies.⁴²

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.

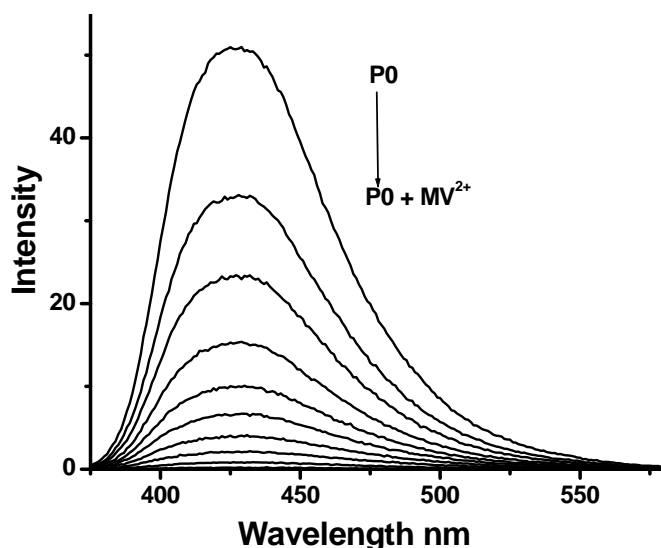


Figure 5. Changes in the emission spectra of **P0** in water at different concentrations of methyl viologen (1) 0 μM , (2) 0.1 μM , (3) 0.2 μM , (4) 0.3 μM , (5) 0.5 μM , (6) 0.7 μM , (7) 1.0 μM , (8) 1.5 μM , (9) 2.5 μM , (10) 4.0 μM . Concentration of **P0** was 1.45×10^{-5} .

The fluorescence spectrum of the polymer **P0** is quenched by the addition of the methyl viologen. The quenching effect is increased by the increase in the concentration of the methyl viologen as shown in Figure 5 and complete quenching was observed by the addition of the 4.0 μM solution of methyl viologen. In very dilute condition, the quenching mechanism increases and I_0/I Vs (Quencher) gives a linear plot.⁴³ We have studied the quenching behaviors of our polymers with MV^{2+} , EV^{2+} , BV^{2+} and cytochrome-c. Figure 6 gave the quenching effect of the polymer fluorescence (**P0**) by the addition of cytochrome-C. The complete quenching of the fluorescence is observed at a concentration of 1.0 μM . Under the low concentrations (lower than 1.0 μM) of the viologen derivatives and cytochrome-c, all the polymers gave a linear relationship of I_0/I vs [Quencher]. The constant K_{SV} for the polymers are tabulated in the table 2. The Stern-Volmer plots for polymer **P0** upon addition of MV^{2+} , EV^{2+} and BV^{2+} are shown in Figure 7.

Among the polymers **P0-P3**, the quenching effects of the polymer fluorescence upon addition of viologen derivatives and Cyt C, **P0**, the polymer without dialkyl chains gave the higher Stern-Volmer constant. The highest K_{sv} value obtained in our systems is by the addition of Cyt C into the polymer **P0**, which is 4.0×10^7 . As there are no dialkyl chains, the interaction of the viologen derivatives with the polymer may be higher, which resulted the efficient quenching of the fluorescence. This is reflected in the case of **P1** and **P2** as well.

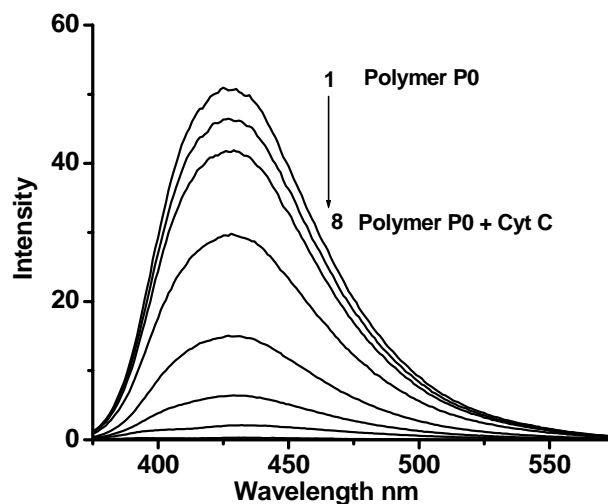


Figure 6. Changes in the emission spectra of **P0** in water at different concentrations of cytochrome-C (1) 0 μM , (2) 0.01 μM , (3) 0.02 μM , (4) 0.05 μM , (5) 0.1 μM , (6) 0.2 μM , (7) 0.5 μM , (8) 1.0 μM , Concentration of **P0** was 1.45×10^{-5} .

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

Polyme r	Quenchers			
	MV	EV	BV	Cyto-C
P0	9.0×10^6	1.0×10^7	2.0×10^7	4.0×10^7
P1	5.1×10^5	6.5×10^5	2.0×10^6	1.0×10^6
P2	4.7×10^5	6.2×10^5	8.1×10^5	9.0×10^5
P3	1.1×10^6	2.0×10^5	9.4×10^5	8.5×10^5

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

The 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 type of the variation of the carbon chain length in the viologen derivatives were reported before for PPV related polymer.³⁴ The reason for such observation may be due to (i) elongation of the side chain increases the collision of the polymer and viologen, (ii) reorganization energy and (iii) the hydrophobicity of the viologen derivatives increases with the chain length.³⁴ The highest K_{sv} value of 4.0×10^7 for the polymer **P0** by the quencher Cyt C is comparable with the previously reported PPV related polymers.³²⁻³⁴

In addition to the viologen derivatives and Cyt C, we also tried the sensing properties for the transition metal ions. Among the metal ions (Co^{2+} , Cu^{2+} , Mg^{2+} , Ag^+ , Li^+ , Cd^{2+} , Gd^{3+} , Al^{3+} , Pr^{3+} , Zn^{2+} , Mn^{2+} and Fe^{3+}) attempted for the sensing properties, only the Fe^{3+} metal ion influence the polymer fluorescence significantly. It indicates that the sulfonate ions prefer the Fe^{3+} metal ion strongly than the other metal ions.

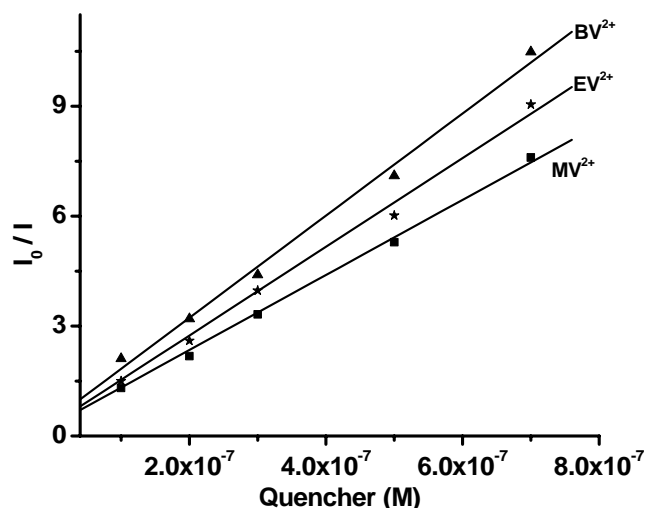


Figure 7. Stern – Volmer plots of the polymer **P0** ($< 1 \mu\text{M}$) quenched by the viologen derivatives: Methyl viologen, MV^{2+} (square), Ethyl viologen, EV^{2+} (star), Benzyl viologen, BV^{2+} (triangle).

IV. CONCLUSIONS

A series of water soluble poly(para phenylenes) with the propoxy sulfonate side chains were synthesized, characterized and their thermal, optical and X-RD properties were studied. Due to the presence of the propoxy sulfonate side chains in the polymers, all the conjugated polymers are soluble in water. The co-polymers consist of the alternating dialkyl substituted phenylene and the propoxy sulfonate substituted phenylene systems. Among the polymers, the polymer **P0** with no alkyl chain groups gave the higher/significant quenching efficiencies with the high value of Stern-Volmer constant by the addition of viologen derivatives and cytochrome-c. Under dilute conditions, the linear Stern-Volmer plots are obtained for all the polymers by the addition of the quencher. At higher concentration, there was a superlinear quenching. The highest K_{sv} of the polymer **P0** by the addition of cytochrome-c is 4.0×10^7 was obtained among all the polymers. The quenching efficiencies increase as 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.

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