

# Molecular Engineering of Amphiphilic Pyridine Incorporated Conjugated Polymers for Metal Ion Sensors

<sup>1</sup>Muthalagu Vetrichelvan, <sup>1,2</sup>Suresh Valiyaveetil\*

Singapore-MIT Alliance, 4 Engineering Drive 3, National University of Singapore, Singapore - 117 576.

**Abstract**—Recent developments in the synthesis and structure-property investigation studies of conjugated polymers have led to the design of novel polymeric materials with tailored properties for advanced technological applications. A promising development in this direction involves the fabrication of conducting polymer based sensors for the detection of metal ions and small organic molecules. Herein, we designed, synthesized and studied a series of amphiphilic copolymers containing alternate phenylene and 2,5- or 2,6- or 3,5-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. Thermal properties, and optical properties of polymers in presence of acid, base and metal ions are investigated. A few target polymers showed high sensitivities for metal ions in solution.

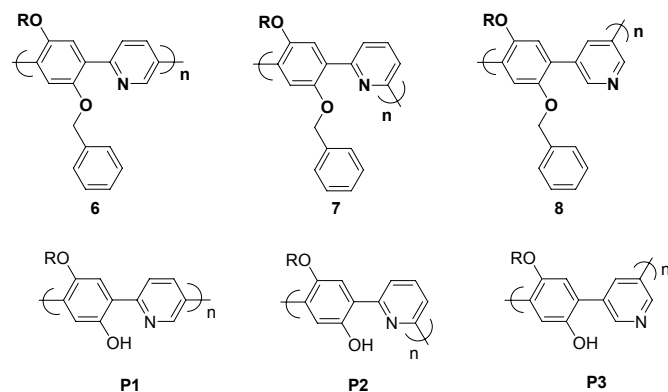
**Index Terms**—conjugated polymer, donor-acceptor system, poly(para phenylene), metal ion sensor.

## I. INTRODUCTION

Conjugated polymers with tunable or switchable physical properties are of interest towards the development of novel materials. Its potential applications include light emitting diodes, thin-film transistors, plastic lasers, chemical sensors, electronic and photonic devices *etc.*<sup>1-8</sup> Pyridine incorporated conjugated polymers and their co-polymers are shown to be better candidates for light emitting devices,<sup>9-14</sup> new tailored luminescent materials and in the area of electron transport studies.<sup>15-18</sup> The use of a donor-acceptor approach can modify the band gap of the polymers and the planarization of polymer backbone by using covalent and secondary interactions (e.g. hydrogen bonding).<sup>11</sup>

Our research efforts are focused on the synthesis and structure-property studies of amphiphilic conjugated polymers (e.g. PPPs).<sup>19</sup> Here, we report the synthesis of conjugated polymers consisting alternate asymmetrically

substituted phenylene and 2,5- or 2,6- or 3,5-substituted pyridine units (Figure 1). Long chain mono-substituted phenyl group has chosen to increase the solubility of the polymer and the hydrogen bonding between the phenolic groups with pyridine nitrogen to planarize the polymer backbone. The optical properties of target polymers can be fine tuned by means of protonation, deprotonation, alkylation and metal complexation. Thermal properties and optical properties of polymers influence of acid and base and metal ion sensing properties are also investigated.



**Figure 1. Structures of precursor (6-8) and target polymers (P1-P3)**

## II. EXPERIMENTAL

### A. Materials and Methods

**Instruments.** The NMR spectra were collected on a Bruker ACF 300 spectrometer with chloroform-*d* or methanol-*d*<sub>3</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. 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

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\* To whom the correspondence should be addressed (email: [chmsv@nus.edu.sg](mailto:chmsv@nus.edu.sg))

<sup>1</sup>Singapore-MIT Alliance, 4, Engineering Drive 3, National University of Singapore, Singapore – 117 576.

<sup>2</sup>Department of Chemistry, 3 Science Drive 3, National University of Singapore, Singapore – 117 543.

powder patterns were obtained using a D5005 Siemens X-ray diffractometer with Cu-K $\alpha$  (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  $40^\circ$ .

**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 nitrogen atmosphere.

### B. Synthesis

Synthetic scheme for the polymers **P1-P3** is shown in scheme-1. 2,5-dibromo hydroquinone (**2**), 2,5-dibromo-4-dodecyloxyphenol (**3**), 2,5-dibromo-1-benzyloxy-4-dodecyloxybenzene (**4**), 1-benzyloxy-4-dodecyloxyphenyl-2,5-bis(boronic acid) (**5**) were synthesized using the procedure reported in the literature.<sup>19</sup>

### General procedure for polymerization of precursor polymers, 6, 7 & 8

The compound diboronic acid, **5** (4.11 g, 9 mmol) and dibromopyridine (2.14 g, 9 mmol) were dissolved in degassed toluene (90 mL) under nitrogen atmosphere. 2 M solution of K<sub>2</sub>CO<sub>3</sub> (60 mL), and tetrakis(triphenylphosphino) palladium(0) (3 mol%, 0.52 g) were added and the mixture was stirred vigorously for 72 hours at 85-90°C, cooled to room temperature and poured into the large excess of methanol. The obtained yellow color polymer was filtered, washed with large amount of water followed by methanol and acetone.

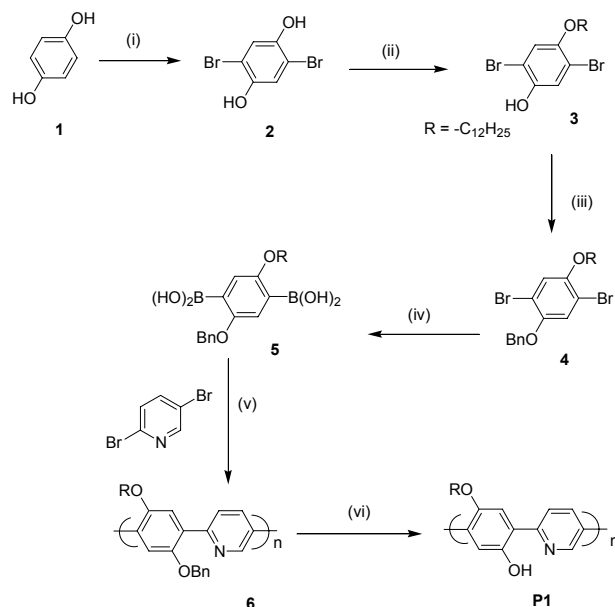
### General syntheses of polymers P1, P2 & P3

Precursor polymer **6** (2.80 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 and the mixture was stirred at room temperature for 48 h, filtered through silicagel/celite and the filtrate was concentrated under reduced pressure. The concentrated solution was poured into excess of methanol (except **P3**). The obtained precipitate was filtered, washed with methanol followed by acetone. In the case of polymer **P3**, the obtained filtrate was concentrated to afford a polymer.

## III. RESULTS AND DISCUSSION

The general synthetic routes toward the monomers and polymers are outlined in scheme 1. The monomer 1-benzyloxy-4-dodecyloxyphenyl-2,5-bis(boronic acid) **5** was synthesized from hydroquinone.<sup>19</sup> 2,5-dibromohydroquinone **2** was obtained by the treatment of bromine in acetic acid. Monoalkylation of **2** with

dodecylbromide in presence of NaOH/EtOH at 40°C gave the compound **3** which was benzylated to get **4**. Then, **4** was reacted with n-butyl lithium followed by quenching with tri-isopropylborate and hydrolysis with hydrochloric acid to afford bis(boronic acid) **5**. All the polymerizations (**6-8**) were done using Suzuki polycondensation.<sup>15,18</sup> Polymers **P1-P3** was prepared by debenzoylation of benzylated precursor polymers **6-8** using 10 % Pd/C under hydrogen atmosphere.



**Scheme 1:** Synthesis of polymers **6** and **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, tri-isopropylborate, 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:

**Table 1. Properties of the target polymers P1-P3**

Polyme r	Color	M <sub>n</sub>	M <sub>w</sub>	PDI	No of AR
P1	Bright Yellow	3265	3883	1.1	26
P2	Yellow	4354	6421	1.4	43
P3	Light brown	3659	5284	1.4	36

M<sub>n</sub> = number average molecular weight, M<sub>w</sub> = weight average molecular weight, PDI = polydispersity, AR = number of aromatic units.

Results of the polymerization reactions are summarized in Table 1. The molecular weights of the precursor polymers were measured by means of gel permeation chromatography (GPC) using THF as eluant and polystyrene as the standards. The molecular weights of the polymers are relatively low with the polydispersity index 1.1-1.4. Similar results were observed for highly functionalized PPPs.<sup>41</sup> The obtained polymers were readily soluble in common organic solvents, such as THF,

chloroform, toluene and trifluoro acetic acid. All precursor polymers (**6-8**) and target polymers **P1-P3** were characterized by FT-IR, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, GPC, and TGA.

### Thermal Properties

The thermal stability of the polymers was evaluated using thermogravimetric analysis (TGA) under nitrogen atmosphere. Precursor polymers **6-8** possess good thermal stability and the onset degradation temperature in the range of 290 - 310° C. This is due to the decomposition of the benzyl group on the polymer side chain. Second onset temperature around 410 - 520° C corresponds to the decomposition of the long alkoxy chain. Thus, two step degradations were observed for the polymers **6-8**. For the target polymers **P1-P3** decomposition temperatures observed around 80 and 220° C; the first decomposition may be due to the evaporation of the entrapped solvent molecules in the polymer lattice.

### Optical properties

#### (a) Absorption and Emission Spectroscopy

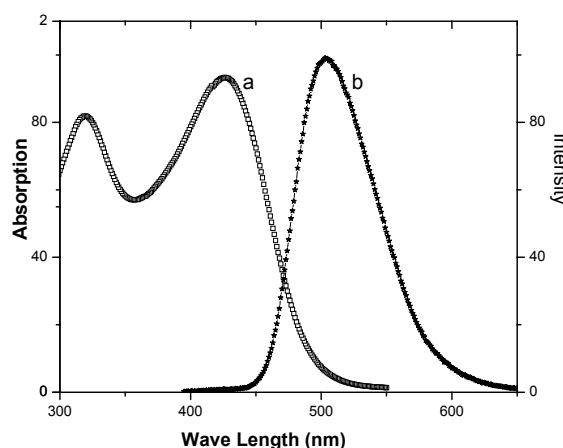
The UV-Vis absorption and fluorescence spectra of precursor polymers **6-8** and target polymers **P1-P3** in solution were studied in chloroform or methanol solution and summarized in Table 2. The optical properties of the polymers in solution depend on the connectivity of the pyridine rings and planarization of the polymer backbone due to hydrogen bonding. All absorption spectra of polymers showed two maxima located in the range of 270-300 and above 300 nm. For polymer **6** and **P1**, the absorption maximum ( $\lambda_{\text{max}}$ ) was observed at 384 and 425 nm respectively. The  $\lambda_{\text{max}}$  for **7** and **P2** is blue shifted to 359 and 362 nm respectively. This is attributed to the low  $\pi$ -electron delocalization on the polymer main chain arising from meta-linkages. The  $\lambda_{\text{max}}$  for **8** and **P3** were further blue shifted to 331 and 302 nm respectively, implying the least  $\pi$ -conjugation length. Similar observations were reported for the long chain dialkyl substituted pyridine incorporated polymer systems.<sup>15</sup>

**Table 2. Absorption and emission wavelength for the polymers**

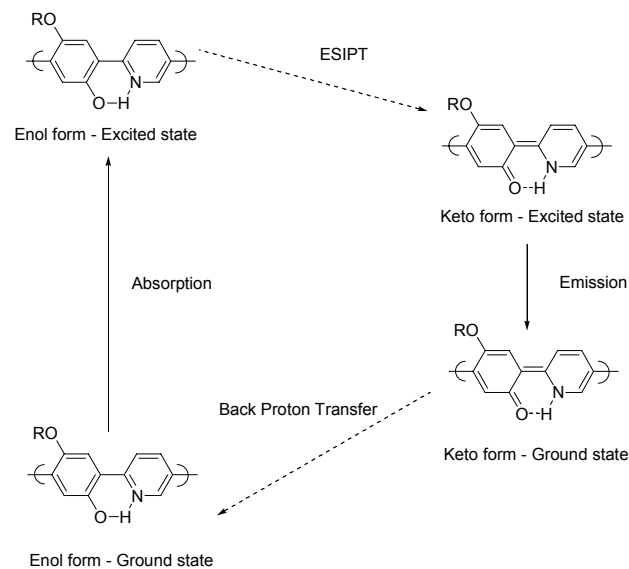
Polymer	Absorption $\lambda_{\text{max}}$	Band gap (eV)	Emission $\lambda_{\text{max}}$	Band gap (eV)
6	384	3.23	431	2.87
7	359	3.45	402	3.08
8	331	3.74	393	3.15
P1	425	2.92	503	2.46
P2	362	3.42	421	2.94
P3	302	4.09	393	3.15

The absorption peaks of the derived target amphiphilic polymers (**P1-P3**) have long absorptions than the corresponding precursor polymers (**6-8**), differ by 4-40 nm. The shift in the absorption of **6** and **P1** polymers was about

41 nm. This large shift of the polymer may be due to the planarization of the polymer backbone due to the intramolecular hydrogen bonding formed between the adjacent phenolic groups with the pyridine nitrogen.



**Figure 3. (a) UV-vis absorption and (b) fluorescence spectra of target polymer, P1**



**Figure 4. Proposed excited-state intramolecular proton transfer for polymer P1**

The emission spectra of the polymers were recorded by exciting the maximum absorption wavelength which was taken from the UV-Vis spectrum. All precursor polymers (**6-8**) were in the blue emitting region and the target polymers are in the blue-green or green region. Figure 3 depicted the absorption and emission spectrum of the polymer **P1**. Polymer **P1** emits in the green region ( $\lambda_{\text{max}} = 503$  nm) with a large Stokes shift of about 78 nm, which may be due to the possibility of excited-state intramolecular proton transfer (ESIPT) as observed in hydrogen bonded oligomers and polymers.<sup>20-22</sup> The proposed intramolecular proton-transfer mechanism for the

polymer **P1** in the electronically excited state is shown in Figure 4. Similar Stokes shift was observed for the remaining polymers. The large Stokes shift for the 3,5-substituted target polymer **P3** may be due to the intermolecular hydrogen bonding on the polymer backbone. Further, polymer **P1** emits at a green region in chloroform (503 nm) and blue in THF solvent (432 nm) at the excitation wavelength of 365 nm.

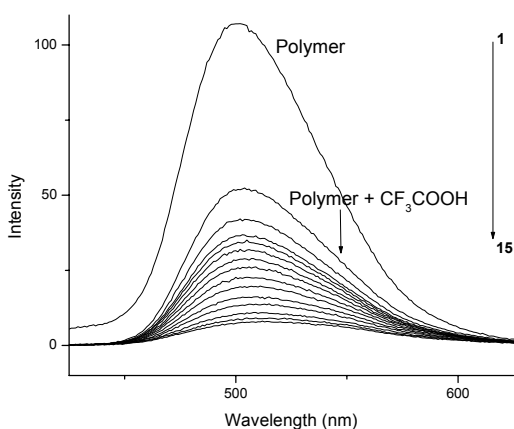
### (b) Protonation and Deprotonation of polymers

The precursor polymers **6-8** and target polymers **P1-P3** are expected to react with protic acids and metal ions. The influences of acid and base on the optical properties of polymers are summarized in Table 3.

**Table 3. Influence of acid and base on the absorption/emission spectra of the polymers**

Polymer	Precursor Polymers			Target Polymers		
	6	7	8	P1	P2	P3
$\lambda_{\max}/E_{\max}$	384/ 433	359/ 402	331/3 93	415/ 503	362/ 420	302/ 392
Protonation ( $\Delta\lambda$ )	29/ 70	8/ 95	12/ 100	10/ 13	5/ 6	6/ 5
Deprotonation ( $\Delta\lambda$ )	a	a	a	45/ 70	10/ 8	6/ 4

a-not expected as there is no free phenolic group



**Figure 5. Changes in the emission spectra of P1 in presence of CF<sub>3</sub>COOH (From 1 to 15, the concentration of CF<sub>3</sub>COOH increasing from 0 to 1000ppm)**

All polymers were effectively protonated with CF<sub>3</sub>COOH. In the case of polymer **6**, the protonation in chloroform leads to red-shift of the  $\lambda_{\max}$  position from 384 to 413 nm resulted  $\Delta\lambda_{\max}$  of 29 and  $\Delta\lambda_{\max}$  of 10 nm was observed for polymer **P1**. This red-shift of the wavelength may be due to the charge transfer from the electron rich phenyl ring to the adjacent electron deficient pyridine ring, which is enhanced by the protonation of the nitrogen.<sup>18</sup> Figure 5

depicts the changes in the fluorescence spectra of the polymer **P1** with increasing concentrations of CF<sub>3</sub>COOH. The emission intensity diminished rapidly with CF<sub>3</sub>COOH concentration and other polymers spectra showed similar changes in the absorption and emission spectrum.

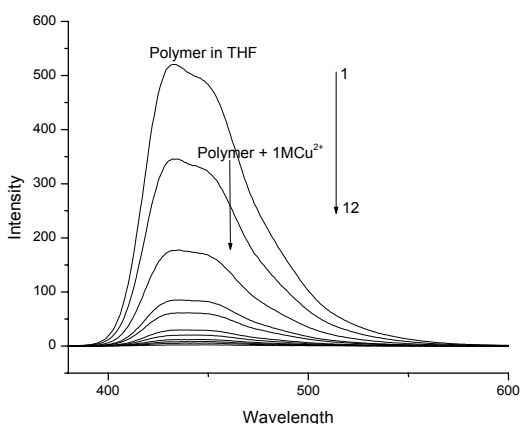
In addition, the amphiphilic polymers **P1-P3** are sensitive to sodium hydroxide due to the presence of phenolic hydroxyl groups on the polymer backbone. There was a large blue-shift in the absorption when the addition of base (1M NaOH, 50 ppm) into chloroform solution of **P1**. This was expected due to the formation of electron rich phenolate anions along the polymer chain. In the case of **P1**, the  $\lambda_{\max}$  position is shifted from 415 to 460 nm. Similar changes in optical properties were reported for pyridine incorporated copolymers.<sup>21</sup> Thus the absorption and emission properties of the polymers can be tuned over a wide optical range by varying the quantity of acid or base added.

### (c) Metal ion sensing properties

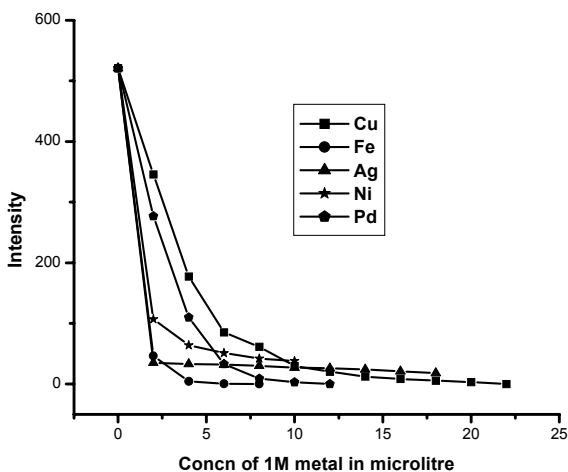
Metal ion sensing properties of the conducting polymers containing bipyridine or phenanthroline systems are reported earlier.<sup>23-25</sup> With the good complexation ability of the pyridine and adjacent phenolic hydroxyl group, the ionochromic effects of the polymers **P1-P3** were studied using alkali, alkaline earth, transition and rare-earth metal ions. The optical ion responsive properties of the polymers were monitored by the addition of methanolic solution of the metal salts into THF solution of the polymers. The apparent metal ionochromic effects of the polymers are the rapid color changes upon the addition of metal ions into the 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 4.

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 different coordination ability of metal ions into the polymer backbone, and stronger coordination induced a larger spectral red shift. Based on the differences in the spectral response, the precursor polymers could sense only selected transition metal ions; in particular Cu<sup>2+</sup> and Fe<sup>3+</sup> only. In the case of polymer **6**, the red-shift in absorption was about 35 and 146 nm upon addition of Cu<sup>2+</sup> and Fe<sup>3+</sup> solutions respectively. Similar influences of these metal ions are observed for the precursor polymers **7** and **8**. For **8**, addition of even 0.2 ppm of metal salts quenched the fluorescence completely which implied particular metal ions could turn-off the fluorescence of the polymers effectively.

The optical properties of target polymers **P1-P3** also 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-P3** showed the ionochromic effects in presence of  $\text{Co}^{2+}$  and  $\text{Ag}^+$  metals (Table 4). Polymer **P1** seems better sensing for 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  $\text{Fe}^{3+}$  solution into the **P1** solution result in a red-shift of 44 and 144 nm respectively. Figure 6 depicted the fluorescence spectra of the polymer **P1** in THF upon adding different amount of  $\text{Cu}^{2+}$ , and the corresponding titration curve is shown in Figure 7 together with additional metal ions for comparison.



**Figure 6. Changes in the emission spectra of P1 in presence of 1M  $\text{Cu}^{2+}$  solution**



**Figure 7. Titration curves of  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  to the polymer P1 in THF solution.**

The complete quenching was observed after the addition of 20  $\mu\text{L}$  addition of  $\text{Cu}^{2+}$  and 8  $\mu\text{L}$  of  $\text{Fe}^{3+}$  solution to achieve complete quenching. In addition, it also showed

changes in  $\lambda_{\text{max}}$  with other transition metal ions like,  $\text{Co}^{2+}$  ( $\Delta\lambda = 15$  nm),  $\text{Ni}^{2+}$  ( $\Delta\lambda = 6$  nm),  $\text{Pd}^{2+}$  ( $\Delta\lambda = 18$  nm),  $\text{Ag}^+$  ( $\Delta\lambda = 11$  nm),  $\text{Mn}^{2+}$  ( $\Delta\lambda = 5$  nm) and  $\text{Zn}^{2+}$  ( $\Delta\lambda = 3$  nm). There are no significant changes with alkali, alkaline earth metals or rare-earth metals.

**Table 4. Absorption responses of P1-P3 upon addition of metal ions.**

		Polymer P1	Polymer P2	Polymer P3
$(\lambda_{\text{max}})$ Ion free		383	360	302
$(\Delta\lambda_{\text{max}})$	$\text{Cu}^{2+}$	44	49	56
	$\text{Fe}^{3+}$	144	114	20
	$\text{Co}^{2+}$	15	4	2
	$\text{Ni}^{2+}$	6	-	-
	$\text{Pd}^{2+}$	18	-	-
	$\text{Mn}^{2+}$	5	-	-
	$\text{Zn}^{2+}$	3	-	-
	$\text{Ag}^+$	11	4	3
	$\text{Mg}^{2+}$	3	-	-
	$\text{Pr}^{3+}$	8	-	-

#### IV. CONCLUSIONS

A novel series of donor-acceptor luminescent conjugated polymers comprising alternating amphiphilic phenylene and pyridine units were synthesized using Suzuki-poly condensation method. All polymers show good solubility towards common organic solvents, such as, chloroform, THF, toluene and trifluoroacetic acid and good thermal properties. Most of the polymers gave strong blue emission in solution. Depending upon the substitution in the pyridine ring (2,5- or 2,6- or 3,5) and the hydrogen bonding, these polymers display a remarkable variation in their optical behavior (absorption and emission). The large Stokes shift in the emission confirmed the possibility of excited-state intramolecular proton transfer (ESIPT) due to intramolecular hydrogen bonding. Protonation, deprotonation of the amphiphilic target polymers by means of acid ( $\text{CF}_3\text{COOH}$ ) and base ( $\text{NaOH}$ ) has significant effect on their optical properties. Addition of acid to the polymer resulted a bathochromic shift and the base gave a hypsochromic effect. All polymers showed metal ion dependence in both absorption and emission maximum ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Ag}^+$ , etc.) In addition to copper and iron, the target polymers **P1-P3** were influenced by the presence of cobalt and silver metal ions. The optical properties of the polymers can be tuned to a large extent by means of protonation, deprotonation and the addition of metal ions.

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## REFERENCES

- [1] Mullen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, Germany, 1998.
- [2] T. M. Swager, The molecular Wire Approach to Sensory Signal Amplification, *Acc. Chem. Res.* Vol-31, pp-201, 1998.
- [3] A. O. Patil, A. J. Heeger, F. Wudl, Optical Properties of Conducting Polymers, *Chem. Rev.* Vol-88, pp-183, 1988.
- [4] U. H. F. Benz, Poly(arylene ethylene)s: Synthesis, Properties, Structures and Applications. *Chem. Rev.* Vol-100, pp-1605, 2000.
- [5] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor-acceptor heterojunctions, *Science.* Vol-270, pp-1789, 1995.
- [6] D. T. McQuade, A. E. Pullen, T. M. Swager, Conjugated Polymer Based Chemical Sensors, *Chem. Rev.* Vol-100, pp-2537, 2000.
- [7] A. Kraft, A. C. Grimsdale, A. B. Holmes, Electroluminescent Conjugated Polymers - Seeing Polymers in a New Light. *Angew. Chem. Int. Ed.* Vol-37, pp-402, 1998.
- [8] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, Electroluminescence in conjugated polymers, *Nature.* Vol-397, pp-121, 1999.
- [9] B. L. Lee, T. Yamamoto, Syntheses of New Alternating CT-Type Copolymers of Thiophene and Pyrido[3,4-*b*]pyrazine Units: Their Optical and Electrochemical Properties in Comparison with Similar CT Copolymers of Thiophene with Pyridine and Quinoxaline. *Macromolecules.* Vol-32, pp-1375, 1999 and refs. therein
- [10] C. G. Bangcuyo, M. E. Rampey-Vaughn, L. T. Quan, S. M. Angel, M. D. Smith, U. H. F. Bunz, Quinoline-Containing, Conjugated Poly(aryleneethynylene)s: Novel Metal and H<sup>+</sup>-Responsive Materials, *Macromolecules* Vol-35, pp-1563, 2002.
- [11] K. Pieterse, J. A. J. M. Vekemans, H. Kooijman, A. L. Spek, E. W. Meijer, Ladderlike Oligomers; Intramolecular Hydrogen Bonding, Push-Pull Character, and Electron Affinity. *Chem. Eur. J.* Vol-6, pp-4597, 2000.
- [12] D. K. Fu, B. Xu, T. M. Swager, Alternating poly(pyridyl vinylene phenylene vinylene)s: synthesis and solid state organizations, *Tetrahedron.* Vol-53, pp-15487, 1997.
- [13] Y. Z. Wang, A. J. Epstein, Interface Control of Light Emitting Devices Based on Pyridine Containing Conjugated Polymers, *Acc. Chem. Res.* Vol-32, pp-217, 1999.
- [14] A. J. Epstein, J. W. Blatchford, Y. Z. Wang, S. W. Jessen, D. D. Gebler, L. B. Lin, T. L. Gustafson, H. L. Wang, Y. W. Park, T. M. Swager, Poly(*p*-pyridine)- and poly(*p*-pyridyl vinylene)-based polymers: Their photophysics and application to SCALE devices, *Synth. Met.* Vol-78, pp-253, 1996.
- [15] S. C. Ng, H. F. Lu, H. S. O. Chan, A. Fujii, T. Laga, K. Yoshino, Blue Electroluminescence from a Novel Donor/Acceptor Polymer Structure. *Adv. Meter.* Vol-12, pp-1122, 2000.
- [16] Y. Z. Wang, D. D. Gebler, D. K. Fu, T. M. Swager, A. G. MacDiarmid, A. J. Epstein, Light-emitting devices based on pyridine-containing conjugated polymers. *Synth. Met.* Vol-85, pp-1179, 1997.
- [17] A. P. Monkman, L. O. Pålsson, R. W. T. Higgins, C. Wang, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, Protonation and Subsequent Intramolecular Hydrogen Bonding as a Method to Control Chain Structure and Tune Luminescence in Heteroatomic Conjugated Polymers. *J. Am. Chem. Soc.* Vol-124, pp-6049, 2002.
- [18] T. Yasuda, T. Yamamoto, Synthesis and Characterization of New Luminescent 1,10-Phenanthroline- and Pyridine-Containing  $\pi$ -Conjugated Polymers. Their Optical Response to Protic Acid, M<sup>n+</sup>, and Solvents, *Macromolecules.* Vol-36, pp-7513, 2003.
- [19] C. Baskar, Y. H. Lai, S. Valiyaveetil, Synthesis of a Novel Optically Tunable Amphiphilic Poly(*p*-phenylene): Influence of Hydrogen Bonding and Metal Complexation on Optical Properties. *Macromolecules.* Vol-34, pp-6255, 2001.
- [20] R. M. Tarakka, X. Zhang, S. A. Jenekhe, Electrically Generated Intramolecular Proton Transfer: Electroluminescence and Stimulated Emission from Polymers, *J. Am. Chem. Soc.* Vol-118, pp-9438, 1996.
- [21] J. C. Penedo, M. Mosquera, F. R. Prieto, Role of Hydrogen-Bonded Adducts in Excited-State Proton-Transfer Processes, *J. Phys. Chem. A.* Vol-104, pp-7429, 2000.
- [22] L. M. Tolbert, K. M. Solntsev, Excited-State Proton Transfer from Constrained System to "Super"photoacids to Superfast proton transfer, *Acc. Chem. Res.* Vol-35, pp-19, 2002.
- [23] B. Wang, M. R. Wasielewski, Design and Synthesis of Metal Ion-Recognition-Induced Conjugated Polymers: An Approach to Metal Ion Sensory Materials, *J. Am. Chem. Soc.* Vol-119, pp-12, 1997.
- [24] T. Yasuda, I. Yamaguchi, T. Yamamoto, A New Soluble 1,10-Phenanthroline-Containing-Conjugated Polymer: Synthesis and Effect of Metal Complexation on Optical Properties, *Adv. Mater.* Vol-15, pp-293, 2003.
- [25] M. Zhang, P. Lu, Y. Ma, J. Shen, Metal Ionochromic Effects of Conjugated Polymers: Effects of the Rigidity of Molecular Recognition Sites on Metal Ion Sensing, *J. Phys. Chem. B* Vol-107, pp-6535, 2003.

**Vetrichelvan M**, received his M.Sc from the ANJA Collge, M. K. University, India in 1998 and Ph.D (Macrocyclic chemistry) from NUS, Singapore in 2003. He is currently working as Singapore-MIT Research Fellow with Assistant Professor Suresh Valiyaveetil. His current research interest includes organic syntheses of oligomers and polymers, macrocyclic chemistry and supramolecular chemistry through single crystal X-ray diffraction.

**Suresh Valiyaveetil** received his M.Sc from Calicut University, India, M. Tech from I. I. Tech, Delhi, India. He received Ph.D from University of Victoria, Canada and completed his post-doctoral research at the Max-Planck, Institute of Polymer research, Mainz, Germany. He worked as a staff-scientist at the Cornell University, Ithaca, NY before joining NUS as Asst. Professor in 1998. His research interests include organic material synthesis, biomaterials, self-assembling systems, polymeric micro-electromechanical systems and nanoscience and technology.