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### BIOCATALYTIC SYNTHESIS OF A RUTHENIUM MACROMOLECULAR COMPLEX FOR PHOTOVOLTAICS

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## BIOCATALYTIC SYNTHESIS OF A RUTHENIUM MACROMOLECULAR COMPLEX FOR PHOTOVOLTAICS\*

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### ABSTRACT

A phenolic ligand, 4-([1,10] Phenanthrolin-5-yliminomethyl)-phenol (APHB) has been synthesized which was subjected to biocatalytic polymerization by Hematin. The polyligand obtained was complexed with Ru[(dcbpy)<sub>2</sub>Cl<sub>2</sub>] (where dcbpy = 4,4'-dicarboxylic bipyridyl) to synthesize a macromolecular complex {Ru[(dcbpy)<sub>2</sub>(APHB)]}<sub>n</sub> (macro dye) for the sensitization of a nanocrystalline titanium dioxide based dye-sensitized photovoltaic cell. The precursor monomeric Ruthenium complex, Ru[(dcbpy)<sub>2</sub>(APHB)] was also prepared for comparison. The overall solar-to-electric conversion efficiency of the macro dye was found to be 0.33%, which is lower than the monomeric complex (1.51%), when a liquid electrolyte is used. The photophysical properties were also measured using UV-visible and luminescence spectroscopy for both the monomeric complex and the macro dye.

*Key Words:* Hematin; Catalytic polymerization; Macro dye; Photovoltaic cell

\*Dedicated to the memory of Professor Sukant K. Tripathy.

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## INTRODUCTION

The search for efficient photosensitizer dyes is a major thrust for the fabrication of low cost nanocrystalline TiO<sub>2</sub> based plastic solar cells. Presently, the most efficient and stable sensitizers are carboxylated Ru(II) polypyridyl complexes.<sup>[1,2]</sup> Though the present polypyridyl Ruthenium complexes have absorption from 400–800 nm, the absorption coefficients above 650 nm wavelengths are very small. The aggregation of these dye molecules is a serious concern in device fabrication. Additionally the fabrication of nanocrystalline TiO<sub>2</sub> solar cells using liquid electrolytes is also a practical problem in the sealing of the cell. Thus, there is a need for designing panchromatic macro dyes incorporating hole transporting conjugated polymers with both strong absorption and minimal aggregation problems. Recently, polythiophenes have been studied as hole conductors as well as sensitizers in solid state dye-sensitized TiO<sub>2</sub> photovoltaic (DSPV) cells.<sup>[3–5]</sup>

Polymers with conjugated backbone have potential applications in molecular electronics such as light emitting diodes and photovoltaics.<sup>[6]</sup> There has been an increasing upsurge of interest in biocatalytic routes of synthesis towards these polymeric backbones of commercial importance. Synthesis of conjugated polymers such as polyanilines<sup>[7]</sup> and polyphenols<sup>[8]</sup> through oxidative coupling by enzymatic catalysis using horseradish peroxidase (HRP)<sup>[9]</sup> in the presence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) has attracted much interest in recent years. Enzymatic polymerization provides not only alternate approaches to chemical synthesis, but also the reaction proceeds under mild and environmentally friendly conditions. Dordick et al.<sup>[10]</sup> also demonstrated that the HRP could catalyze polymerization of phenolic monomers in mixed organic solvent systems. Since then, several modified enzymatic reaction systems such as reverse micelles,<sup>[11]</sup> Langmuir monolayers<sup>[12]</sup> and template assisted synthesis<sup>[13]</sup> have also been investigated. The prohibitive cost of the enzyme peroxidase coupled with its limited activity in organic solvents has urged on the need for more cost-effective and robust alternatives. Subsequently Akkara et al.<sup>[14]</sup> proposed a hydroxy ferriprotoporphyrin, Hematin, the catalytic center of certain enzymes, as catalyst for synthesis of polyaromatic compounds. The studies on Hematin catalyzed polymerization put forward the theory that the iron in Hematin can also undergo a cycle of redox changes similar to HRP in the presence of H<sub>2</sub>O<sub>2</sub> and it was proved to be a suitable catalyst in aqueous media (at high pH) and in even organic solvents such as DMF. We thus considered employing this low-cost compound in our polymerization schemes, in the process; explore the versatility and synthetic ability of this catalyst.

The objective of this study was primarily to synthesize a macro dye based on a Ruthenium bipyridyl complex for photovoltaic applications. Our

group recently reported the synthesis of macro dyes such as poly(4-phenylazophenol),<sup>[15]</sup> poly(hydroxystilbene)<sup>[16]</sup> using HRP as a catalyst. The macro dyes synthesized by enzymatic catalysis essentially have 100% dye content with unusual articulated structure. In this study, we have extended this concept of macrodye synthesis with the aim of developing efficient dye-sensitized TiO<sub>2</sub> solar cells. We thus present here the synthesis and characterization of a 5-aminophenanthroline based phenolic ligand and its biocatalytic polymerization with Hematin. The preparation of a Ruthenium macromolecular complex using the poly ligand and the synthesis of a precursor monomeric Ruthenium complex are described. The photophysical and photovoltaic properties of both the monomer and the macro dye are also reported in this paper.

## EXPERIMENTAL

### Materials and Measurements

Hematin was purchased from Sigma Chemical Co. (St. Louis, MO). 4-hydroxybenzaldehyde, RuCl<sub>3</sub>·3H<sub>2</sub>O and 4,4'-bipyridyl dicarboxylic acid were purchased from Aldrich Chemical Co. and were used as received. 5-amino-1,10-phenanthroline was purchased from PolySciences and N3 was purchased from Solaronix. The infrared spectra were measured on a Perkin-Elmer 1720 FT-IR spectrometer. The UV-visible absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer. Fluorescence spectra were measured on a Perkin-Elmer LS-55. <sup>1</sup>H-NMR spectra were obtained on a Bruker ARX-500 MHz FT-NMR spectrometer.

TiO<sub>2</sub> films were prepared using commercial colloidal TiO<sub>2</sub> powder (Degussa, P25, average size 10–50 nm) by spin coating method onto SnO<sub>2</sub>:F coated glass plates. The TiO<sub>2</sub> films were then sintered at 500 °C for 1 h. Adsorption of the dye was carried out by placing the sintered hot (about 80 °C) TiO<sub>2</sub> film into the dye solution (10<sup>-4</sup> M) in ethanol and soaking it for overnight. On completion of the dye adsorption the film was rinsed with ethanol and dried and the PV measurements were performed immediately. This involved an assembly in which the DSPV cells were clamped on a platinum coated SnO<sub>2</sub> counter electrode and the dye adsorbed TiO<sub>2</sub> working electrode with active area of 0.25 cm<sup>2</sup>. A liquid electrolyte consisting of 1.0 M LiI and 0.1 M I<sub>2</sub> in acetonitrile was introduced in between the two plates. The DSPV cells were exposed to simulated AM1.5 solar light at 1 sun of 100 mW/cm<sup>2</sup> light intensity using an Oriel 1000 W xenon lamp and appropriate filters. Photocurrents and photovoltages were measured using a Keithley 2400 source meter in conjunction with a personal computer.

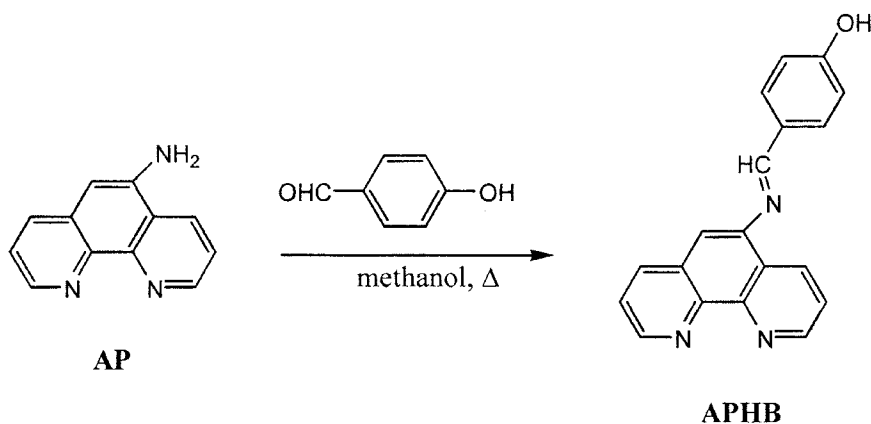
### Synthesis Procedures

#### Synthesis of 4-([1,10]Phenanthrolin-5-yliminomethyl)-Phenol (APHB)

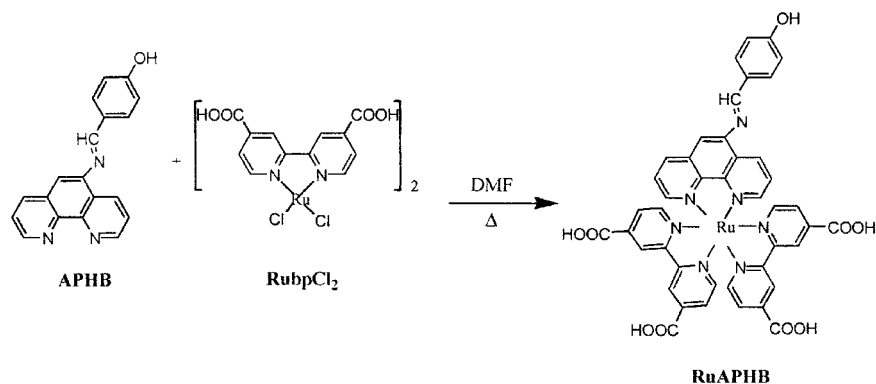
The synthesis of APHB is shown in Scheme 1. To a warm solution of 0.1 g of 5-amino-1,10-phenanthroline in 25 mL of methanol, 0.062 g of 4-hydroxybenzaldehyde dissolved in 5 mL of methanol was added drop wise under  $N_2$  atmosphere. The reactants were heated to reflux for 5 h and cooled to room temperature. The precipitate obtained was filtered and washed several times with methanol to obtain 0.12 g of a yellow solid, 4-([1,10]Phenanthrolin-5-yliminomethyl)-phenol (APHB). The product was recrystallized from N, N-dimethylformamide/ether. FTIR (KBr pellet):  $3428\text{ cm}^{-1}$  (OH stretching),  $3070\text{ cm}^{-1}$  (aliphatic C-H),  $1601, 1576\text{ cm}^{-1}$  (C=C stretching), UV-vis absorption:  $\lambda_{\text{max}}$  at 340 nm in ethanol solution;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  10.3 (s, 1H),  $\delta$  9.1 (d, 1H),  $\delta$  9.0 (d, 1H),  $\delta$  8.8 (d, 1H),  $\delta$  8.7 (s, 1H),  $\delta$  8.4 (d, 1H),  $\delta$  7.9 (d, 2H),  $\delta$  7.7 (m, 2H),  $\delta$  7.6 (s, 1H),  $\delta$  6.9 (d, 2H).

#### Synthesis of $\text{Ru}[(\text{dcbpy})_2(\text{APHB})]$ (RuAPHB)

The synthesis of RuAPHB is shown in Scheme 2. 0.1 g of  $\text{Ru}[(\text{dcbpy})_2\text{Cl}_2]$  ( $\text{Ru}(\text{bpyCl}_2)$ ) was dissolved in 20 ml of N,N-dimethyl formamide (DMF) and to this solution 0.05 g of APHB was added and refluxed for 6 h under  $N_2$  atmosphere. After standing overnight, the resulting orange-red colored precipitate was filtered and washed several times with acetone to give 0.055 g of RuAPHB. FT-IR (KBr pellet):  $3428\text{ cm}^{-1}$  (OH stretching),  $2943\text{ cm}^{-1}$  (aliphatic C-H),  $1614\text{ cm}^{-1}$  (C=C stretching), UV-vis absorption:  $\lambda_{\text{max}}$  at 466 nm in DMF solution;  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  8.8 (d, 2H-bp),  $\delta$  8.7 (s, 2H-bp),  $\delta$  7.6 (d, 2H-bp),  $\delta$  8.6 (d, 1H-ap),  $\delta$  8.2 (d, 1H-ap),



**Scheme 1.** Synthesis of phenolic ligand, APHB.

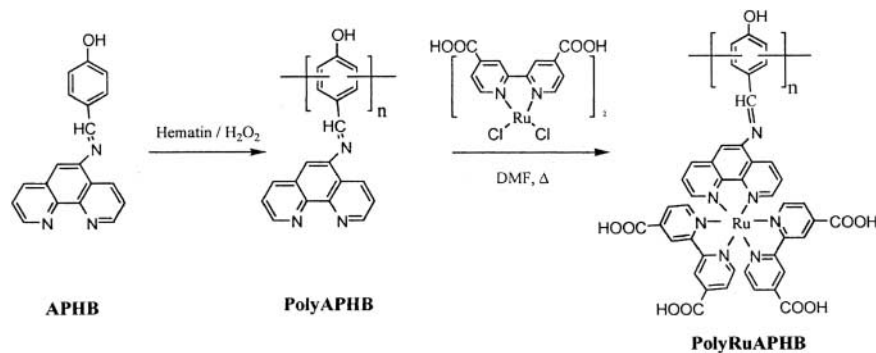


*Scheme 2.* Synthesis of monomeric complex, RuAPHB.

$\delta$  8.1 (d, 1H-ap),  $\delta$  7.9 (d, 1H-ap),  $\delta$  7.9 (s, 1H-ap),  $\delta$  7.7 (d, 1H-ap),  $\delta$  7.6 (m, 2H-ap),  $\delta$  7.4 (d, 2H-ap),  $\delta$  7.4 (s, 1H-ap),  $\delta$  7.3 (s, 1H-ap) where bp = 4,4'-dicarboxylic bipyridyl ligands and ap = 5-amino-1,10-phenanthroline ligand.

### Polymerization of APHB

The synthesis of the macrodye PolyRuAPHB was accomplished in two steps; Hematin catalyzed polymerization of APHB followed by the complexation as shown in Scheme 3. The ligand, APHB (0.02 g) was dissolved in 5 mL of DMF by sonication. To this solution was added a catalytic amount (4 mg) of Hematin followed by the drop wise addition of 30% H<sub>2</sub>O<sub>2</sub> (3 mL). The solution turned red on addition of the peroxide accompanied with vigorous evolution of oxygen. The reaction was allowed to proceed till completion and the solvent evaporated off under high vacuum. Repeated washings with ice-cold water-methanol were carried out to remove the traces



*Scheme 3.* Synthesis of polymeric ligand (PolyAPHB) and macro dye (PolyRuAPHB).

of DMF and the dark colored solid obtained was recrystallized with acetone to yield 0.01 g of the pure polymer, PolyAPHB. FT-IR (KBr):  $3428\text{ cm}^{-1}$  (OH stretching),  $2943\text{ cm}^{-1}$  (aliphatic C-H),  $1663\text{ cm}^{-1}$  (C=C stretching), UV-vis absorption (DMF solution):  $\lambda_{\text{max}}$  at 340 nm and a new peak appeared at 526 nm.  $^1\text{H}$  NMR: broad and featureless from 7–9 ppm.

#### Synthesis of $\{\text{Ru}[(\text{dcbpy})_2(\text{APHB})]\}_n$ (PolyRuAPHB)

The polyAPHB (0.01 g) obtained was dissolved in 5 ml of DMF and further complexation was carried out by adding 0.01 g of  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  dissolved in 5 ml of DMF followed by refluxing the solution overnight. A dark colored precipitate (0.014 g) obtained was filtered off and washed several times with acetone and methanol. The polymer, PolyRuAPHB was characterized by UV-vis, FTIR and  $^1\text{H}$  NMR spectroscopy. FT-IR (KBr pellet):  $3428\text{ cm}^{-1}$  (OH stretching),  $2943\text{ cm}^{-1}$  (aliphatic C-H),  $1701\text{ cm}^{-1}$  (C=O stretching),  $1614\text{ cm}^{-1}$  (C=C stretching); UV-vis absorption:  $\lambda_{\text{max}}$  at 476 nm in ethanol solution;  $^1\text{H}$  NMR: broad and featureless from 7–9 ppm.

## RESULTS AND DISCUSSION

The Hematin-catalyzed polymerization of 4-ethylphenol in a buffer solution of pH 11.0 has been earlier reported by Akkara et al.<sup>[14]</sup> It was proposed that the iron group in Hematin interacted with hydrogen peroxide, resulting in changes in the oxidation state of iron, and which subsequently reacts with the substrate in a one-electron transfer reaction to produce the substrate radical and a new iron-heme complex. These substrate radicals consequently couple to form the polymer. There has also been another report on Hematin catalyzed vinyl polymerizations in aqueous media by Singh et al.<sup>[17]</sup> however only low molecular weight polymers were obtained with the former compared to HRP.

We have tried to explore the possibility of polymerization of the aforementioned monomeric ligand both in aqueous media, as well as organic media using HRP and Hematin, respectively. No polymerization was observed in the case of HRP in aqueous media, which led us to investigate Hematin as an additional option. Hematin was found to be catalytically active in organic solvents and could efficiently catalyze the polymerization in dimethylformamide. Thus, in the present study we have carried out the polymerization of APHB in organic media in order to gain improved yields over a short period of time.

Figure 1 shows the combined FT-IR spectra of the monomeric ligand (APHB), polyligand (PolyAPHB) as well as the polymeric ruthenium complex (PolyRuAPHB). The Hematin catalyzed polymerization of phenolic

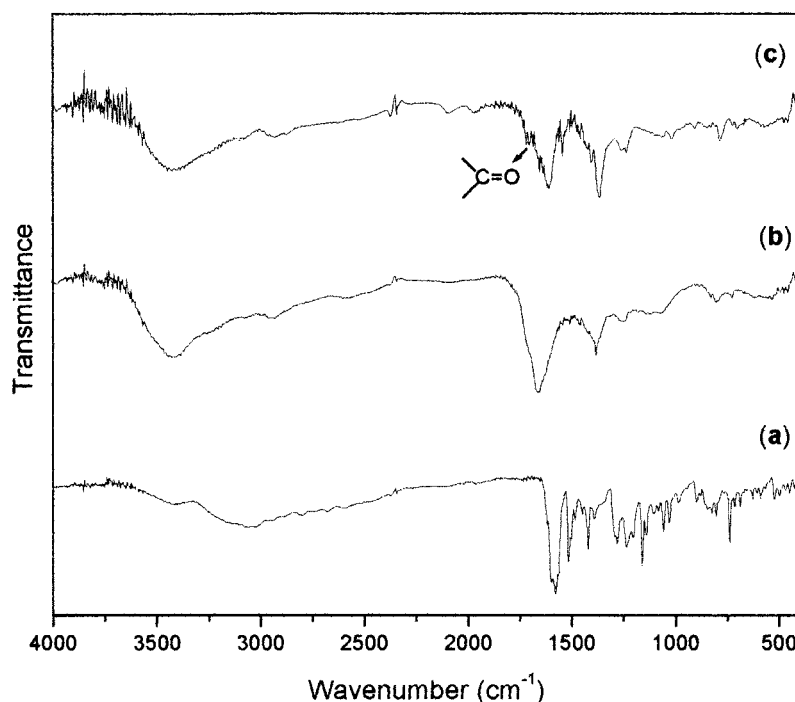


Figure 1. FT-IR spectrum of (a) APHB, (b) PolyAPHB, and (c) PolyRuAPHB.

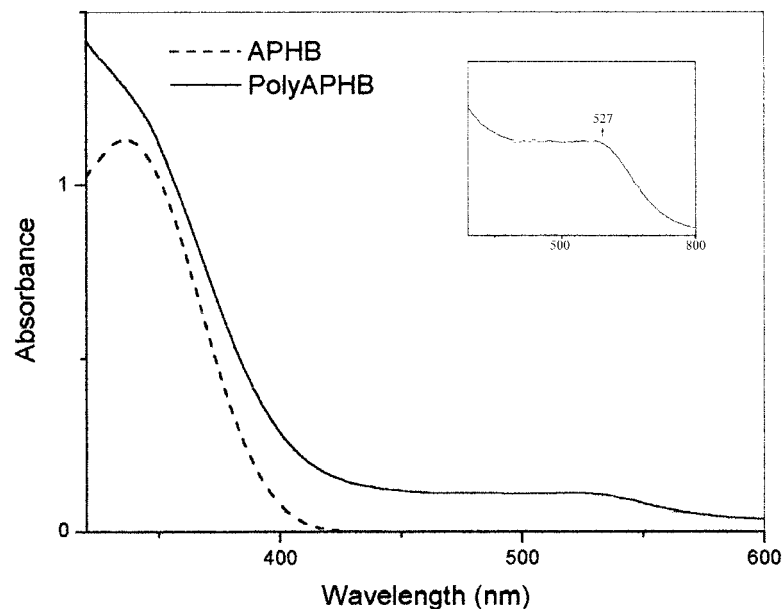
compounds has been observed in previous reports to usually produce mixture of polymers with complicated structures similar to peroxidase-catalyzed polymers.<sup>[18]</sup> Analogous to the macrodyes synthesized using HRP, the FTIR spectra of the polymer, PolyAPHB shows broad peaks around 3300–3000 cm<sup>-1</sup> attributed to the OH stretching and internal hydrogen bonding.<sup>[19]</sup> The retention of a strong OH stretch region in the polymer suggests that most of the OH groups in the monomer are not involved in the coupling reaction and that the resulting polymer has significant phenol functionality. Due to the presence of the para substituted group at the phenyl ring, the vibrational stretching frequency ranging from 1700–600 cm<sup>-1</sup> is broad and thus complicated to analyze. The spectra of PolyRuAPHB shows a weak peak at 1701 cm<sup>-1</sup> due to carbonyl of carboxylic acid groups that are present on the bipyridyl ligand.

The <sup>1</sup>H-NMR spectra of the monomers show very sharp peaks compared to the broad peaks present in the spectrum of the polymer. This broadening of the proton NMR resonance peaks is attributed to polymerization and has been previously observed with numerous other enzymatically prepared polyphenol systems.<sup>[20]</sup> The <sup>1</sup>H-NMR spectra of the PolyAPHB and PolyRuAPHB are essentially featureless with a broad peak ranging from 7 ppm to 9 ppm assigned to the aromatic protons. This unusual

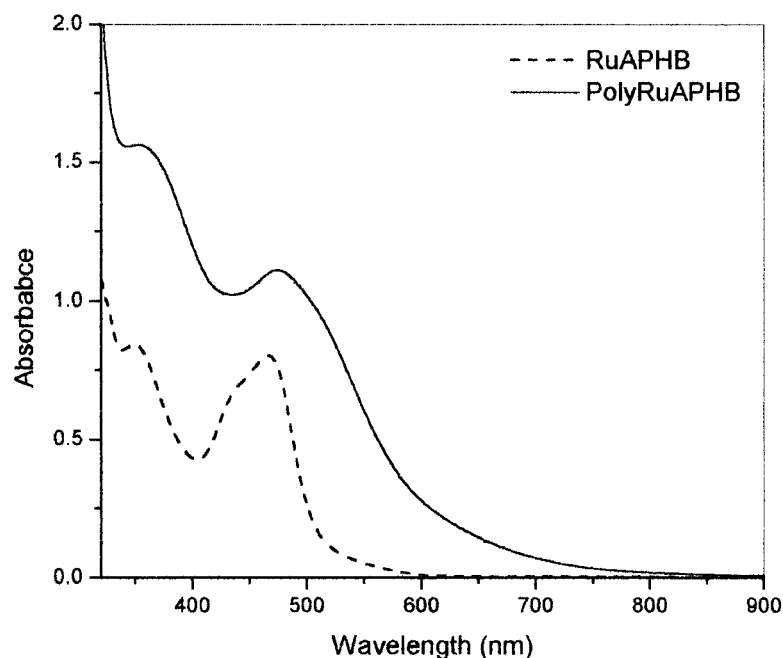


broadening can be attributed to either the high molecular weight or the broad distribution of the resulting polymers proposed in previous studies.<sup>[20]</sup> However, the evident disappearance of ortho protons on the phenol ring implied that the most favored coupling takes place at ortho positions of the phenol ring in catalytic polymerization.

Figure 2 shows an evaluation of the UV-visible absorption spectra of the monomeric ligand (APHB) and polymer (PolyAPHB). The spectrum of the ligand APHB exhibited absorption maxima at 340 nm which was retained in the polymer also. However, a weak and broad peak from 450–575 nm was also observed in the PolyAPHB spectrum which was attributed to the increase in conjugation due to coupling between aromatic rings. The spectra of the monomeric complex (RuAPHB) and its successor polymeric complex (Poly-RuAPHB) are shown in Fig. 3. The peak at 466 nm in RuAPHB was owing to the metal-to-ligand charge transfer (MLCT) band which is also present in the polymer but red shifted to 476 nm. The peak at 350 nm was assigned to the  $\pi$ - $\pi^*$  transition within the ligands (5-amino-1, 10-phenanthroline and 4,4'-dicarboxylic bipyridyl ligands). The comparable absorption spectrum of poly-RuAPHB compared to RuAPHB suggests that the incorporation of the Ruthenium in the Polyligand (PolyAPHB) was successful. It is indeed interesting to note that the absorption of cutoff wavelength was extended to 800 nm in the polymer compared to the RuAPHB (600 nm). This was an encouraging result from the point of view of efficient light harvesting in near-IR region.



**Figure 2.** UV-visible spectra of APHB and PolyAPHB measured in DMF solution (inset shows magnified 420–600 nm region).



*Figure 3.* UV-visible spectra of RuAPHB and PolyRuAPHB measured in DMF solution.

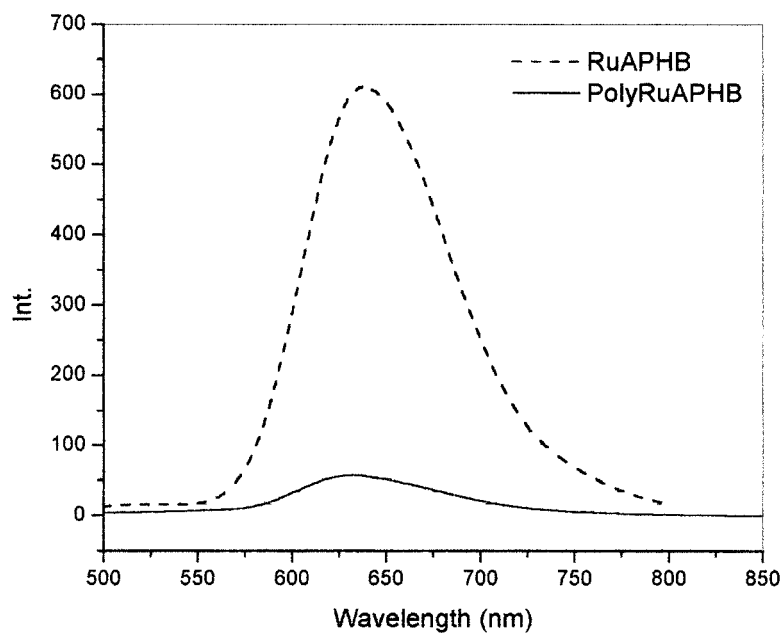
The fluorescence spectrum of RuAPHB and the final polymeric complex PolyRuAPHB are shown in Fig. 4. As typically expected, the polymerization of fluorescent chromophores resulted in decreased fluorescence due to increased local concentration quenching effect.<sup>[21]</sup>

The current-voltage (I-V) curves measured for RuAPHB and PolyRuAPHB are shown in Fig. 5. The short circuit current density ( $I_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF) and overall efficiency ( $\eta_e$ ) for all the dyes are presented in Table 1.

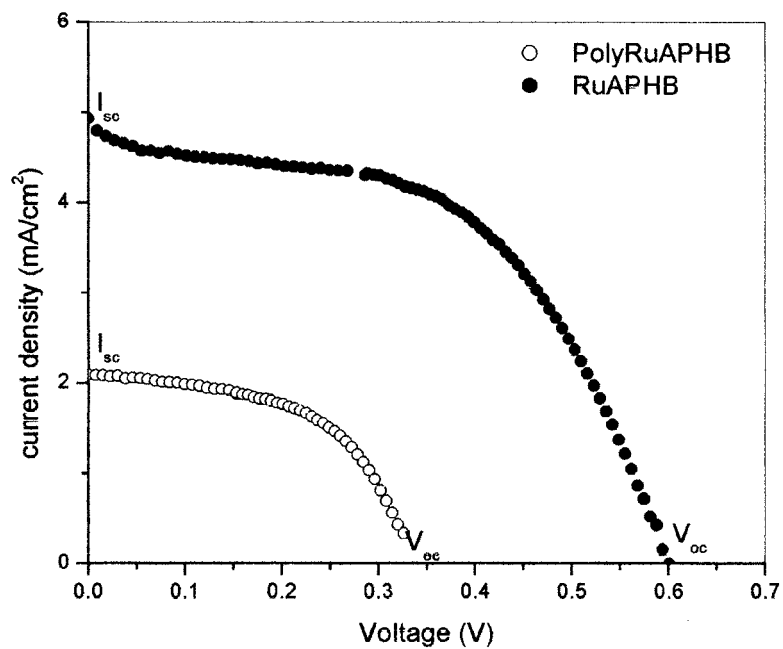
The PV properties of both RuAPHB and PolyRuAPHB have been compared with a well known and standard dye, N3 in Table 1. The monomeric complex, RuAPHB is observed to exhibit half of the overall efficiency of N3. However, the overall efficiency of macro dye sensitized cell was lower compared to RuAPHB. The considerable conversion efficiency of this macro dye opens up a new class of macro sensitizers and helps in further design of biologically derived macro dyes for the development of molecular solar cells.

## CONCLUSION

A new class of Ruthenium complex based macro dye was synthesized via novel polymerization route employing Hematin as an efficient biocatalyst. The MLCT absorption profile of the polymer complex is seen to extend into



**Figure 4.** Fluorescence spectra of RuAPHB and PolyRuAPHB (excited at 476 nm) measured in DMF solution.



**Figure 5.** Current-voltage (I-V) curves measured for RuAPHB and PolyRuAPHB.

**Table 1.**  $I_{sc}$ ,  $V_{oc}$ , FF and  $\eta_e\%$  Obtained from Current Voltage Measurements for the Dyes RuAPHB, PolyRuAPHB, and a Standard Dye, N3

Dye	$I_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (mV)	FF	$\eta_e\%$
RuAPHB	5.5	580	0.48	1.51
PolyRuAPHB	2.1	340	0.48	0.33
N3	10.4	550	0.52	2.99

visible and near IR region giving rise to possibilities of a novel and versatile class of light harvesting dyes. The photovoltaic overall efficiency of the polymeric complex (0.33%) is found to be lower than the monomeric complex (1.51%). However, the considerable efficiency observed in the polymer is encouraging from the view of concept of using macro dyes in photovoltaic cells. We are currently investigating detailed structural features of the Poly-RuAPHB and further synthesis of pure organic macro dyes is in progress in order to unravel the structure-activity relationships for optimizing the solar cell efficiency.

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