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Biocatalytic synthesis of novel electronic and photovoltaic materials*

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Abstract: A new class of ruthenium complex-based macrodye and a dinuclear complex were synthesized via a biocatalytic route employing hematin as an efficient biocatalyst. The photovoltaic overall efficiency of the dinuclear complex was found to be 2.1 % and higher than the polymeric complex (0.33 %). Furthermore, we have developed an environmentally benign methodology for the synthesis of novel pegylated polyphenolics. The reaction conditions used do not require any organic solvents, and all the reactions were performed in aqueous media. The synthesized polymers were soluble in both organic and aqueous media, and provide further opportunity to tailor the properties. Finally, a novel biomimetic method for the synthesis of a conducting molecular complex of polypyrrole and of thiophene substitute in the presence of a polyelectrolyte, such as polystyrene sulfonate (SPS), is presented. A synthetic enzyme based on hematin was used to catalyze the polymerization of pyrrole (PYR) and 3,4-ethylenedioxythiophene (EDOT) in the presence of SPS. Copolymers of EDOT and PYR have also been synthesized, and these novel materials have been shown to exhibit high electrical conductivity.

INTRODUCTION

The search for efficient photosensitizer dyes is a major thrust for the fabrication of low-cost nanocrystalline TiO_2-based plastic solar cells. Presently, the most efficient and stable sensitizers are carboxylated Ru(II) polypyridyl complexes [1–2]. Though the present polypyridyl Ru complexes have absorption from 400–750 nm, the absorption coefficients above 650 nm are very small. The aggregation of these dye molecules is a serious concern in device fabrication. Additionally, the fabrication of nanocrystalline TiO_2 solar cells using liquid electrolytes is also a practical problem in the sealing of the cell. Thus, there is a need for designing panchromatic macrodyes incorporated into hole-conducting conjugated polymers with both strong absorption and minimal aggregation problems. The objective of this study was to synthesize macrodyes and dinuclear complexes based on a Ru bipyridyl complex and biocatalytically synthesized ligands for photovoltaic applications. Our group recently reported the synthesis of macrodyes such as poly(4-phenylazophenol) [3] and poly(hydroxystilbene) [4] using horse-

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radish peroxidase (HRP) as a catalyst. The macrodyes 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_2 solar cells. A variety of bridging ligands were used toward preparation of multinuclear systems with extended conjugation. Among them, the recently developed tetrapyrido [3,2-a:2',3'-c:3",2"-h:2'",3'"-j]phenazine (tpphz) is a very interesting bridging ligand owing to its favorable structural features [5].

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 Ru macromolecular complex using the poly ligand is described.

Furthermore, the focus of our laboratory is also the development of readily processable conducting polymers and polyelectrolytes having high ionic conductivity and stability through biocompatible processes [6–7]. We anticipated that very high ionic conductivity in polymer-ion complexes is attainable by designing polymer systems with oligomeric poly(ethylene glycol) (PEG) chains tethered to very irregularly arranged polymer chain, to reduce the crystallization of PEG. Such a system is expected to provide very high free volume, resulting in good segmental mobility while maintaining good mechanical properties. Moreover, such a polymer system should be very inexpensive and environmentally stable.

Enzymes have proven to be powerful catalysts for the polymerization of a wide variety of monomers and macromonomers. They represent a family of "environmentally friendly" natural catalysts that can function under mild reaction conditions. HRP is an oxido-reductase that acts on hydrogen peroxide and/or alkyl peroxide as an oxidant and polymerizes several reducing substrates such as phenol, hydroquinone, pyrogallol, catechol, aniline, and *p*-aminobenzoate. The oxidative coupling of a variety of substrates such as phenols and aromatic amines catalyzed by HRP in the presence of hydrogen peroxide has been reported. Recently, we have designed and developed [8–9] methodologies on lipase (*Candida antarctica* lipase B), oxidase (HRP), and their combination for the synthesis of copolymers of PEG with various phenolic monomers.

Herein, we report the HRP-mediated synthesis of pegylated polyphenolics and optimization of reaction conditions to get high-molecular-weight polymers.

Moreover, encouraged by the numerous reports based on the common scenario of Fe^{2+} catalysts, we have investigated the prospect of biomimetic catalysts, which would effectively simulate the action of enzymes, but offer greater stability and lower cost in a similar eco-friendly manner. We thus have explored the use of hematin, which serves as a catalytic center of redox enzymes such as catalase, cytochrome C, etc. There have been reports of the use of different forms of hematin for catalysis, in aqueous conditions, but the catalytic activity was observed to be much lower than that of the enzyme [10–12]. Additionally, Akkara et al. reported the efficient synthesis of polyaromatic compounds catalyzed by hematin in mixed solvent systems or buffer systems of high pH values [13]. We had previously reported the use of a chemically modified hematin called poly(ethylene glycol)-hematin (PEG-hematin) functioning as a "syn-enzyme" to effectively synthesize conducting polyaniline in the presence of polyelectrolye templates [14]. We report here further modification of this artificial catalyst toward the synthesis of conducting poly-3,4-ethylenedioxythiophene (PEDOT) and polypyrrole (PPYR) with the ultimate goal of expanding the versatility of this catalyst and to use these conductive polymers as cathodes in the photovoltaic cell.

Additionally, a unique template-assisted approach for the synthesis of water-soluble polymers has been reported from our laboratories involving the enzymatic polymerization of aniline and phenol with HRP as the catalyst in the presence of an anionic polyelectrolyte [6–7]. In this case, the polyelectrolyte, such as polystyrene sulfonate (SPS), serves several functions, namely, enabling the electrostatic alignment of the aniline monomers to promote a *para*-directed coupling, provides counterions for maintaining charge neutrality in the doping process and complexes with the polymer to maintain water solubility. Aside from the polyelectrolyte macromolecular templates, micellar templates such as sodium dodecylbenzene sulfonic acid and biological templates like DNA were also investigated. These tem-

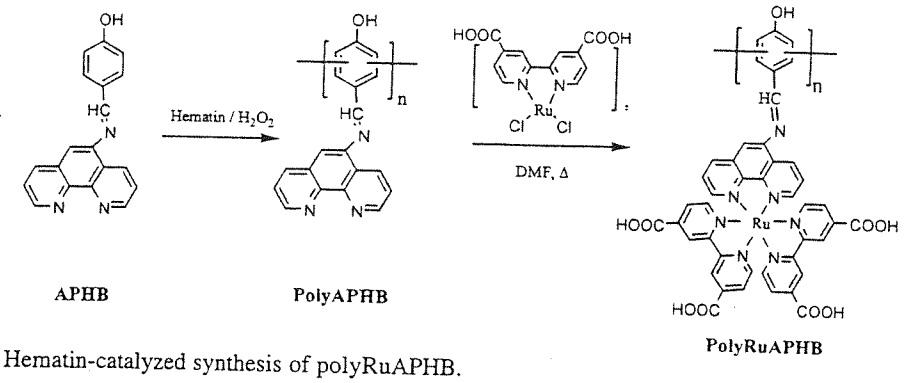
plates have been reported to be successful as nanoreactors in the one-pot enzymatic synthesis of conducting polyanilines [15]. Thus, the template provided a "local" environment wherein the pH and the charge density near the template molecule were different from that of the bulk solution.

In this paper, we report a novel synthesis of water-soluble PEDOT and PPYR using PEG-hematin as an efficient catalyst in the presence of SPS as a template.

MATERIALS AND METHODS

Hematin was purchased from Sigma Chemical Co. (St. Louis, MO). 4-Hydroxybenzaldehyde, $RuCl_3 \cdot 3H_2O$ and 4,4'-bipyridyl dicarboxylic acid were purchased from Aldrich Chemical Co. and were used as received. 10-Aminophenanthroline was purchased from PolySciences, and N3 was purchased from Solaronix. HRP was purchased from Sigma. All other chemicals were purchased from Aldrich and used as received unless otherwise specified.

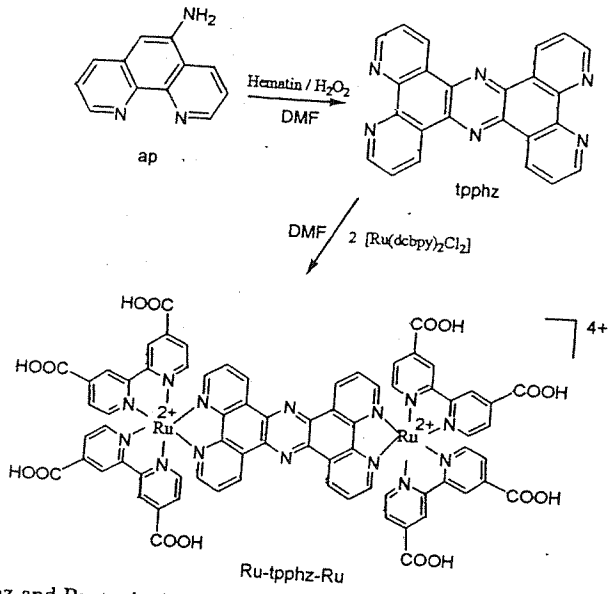
The synthesis of the macrodye polyRuAPHB [16] was accomplished in two steps; hematin-catalyzed polymerization of 4-([1,10]phenanthrolin-5-yliminomethyl)-phenol (APHB) followed by the complexation with $Ru(dcbpy)_2Cl_2$ as shown in Scheme 1.



Scheme 1 Hematin-catalyzed synthesis of polyRuAPHB.

We have synthesized tpphz and a dinuclear Ru complex using hematin as a biocatalyst. The synthesis of the dinuclear complex was accomplished in two steps; hematin-catalyzed synthesis of tpphz followed by the complexation as shown in Scheme 2.

The synthesis of tpphz and Ru-tpphz-Ru followed the procedure reported earlier. UV–vis (ethanol) λ_{max} 454 nm; CHN anal. calc. for $C_{68}H_{48}Cl_2N_{14}O_8Ru_2$ $2Cl^-$. $2H_2O$: C, 54.51; H, 3.50; N, 13.09; found: C, 55.04; H, 3.05; N, 13.05.



Scheme 2 Synthesis of tpphz and Ru-tpphz-Ru.

TiO_2 films were prepared using commercial colloidal TiO_2 powder (Degussa, P25, average size 10–50 nm) by spin-coating method onto SnO_2:F-coated glass plates. The TiO_2 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_2 film into the dye solution (10^{-4} M) in ethanol and allowed to soak 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 dye-sensitized photovoltaic (DSPV) cells were clamped on a platinum-coated SnO_2 counter electrode and the dye-adsorbed TiO_2 working electrode with active area of 0.25 cm^2. A liquid electrolyte consisting of 1.0 M LiI and 0.1 M I_2 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^2 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.

The general method for enzymatic polymerizations of the pegylated polyphenolics was the following: To a solution of 4-pegyloxymethyl phenol (0.070 mole) in sodium phosphate buffer (pH 4.75, 20 ml), 10 mg of HRP was added. The reaction vial was kept at 25 °C and the polymerization reaction was initiated by the addition of 4 ml of 0.03 % hydrogen peroxide (added in small increments of 200 µl). The reaction was monitored by thin-layer chromatography using a gradient solvent system of ethyl acetate in petroleum ether. After completion, the reaction was quenched by the addition of 5 ml of acetone, and any precipitate obtained was filtered. The filtrate so obtained was concentrated and redissolved in water and dialyzed against water using a molecular-weight cut-off of 1000. After dialysis, the solution was freeze-dried and used for further analysis.

The polymerization of pyrrole (PYR) or 3,4-ethylenedioxythiophene (EDOT), in the presence of SPS was catalyzed by PEG-hematin [17] at 25 °C using hydrogen peroxide under ambient conditions. 36.8 mg of SPS was dissolved in deionized water (10 ml) at pH 1.0 for the polymerization of EDOT (concentration 0.2 mM) and at pH 2.0 for the polymerization of PYR (0.2 mM). This was followed by the addition of 5 mg of PEG-hematin to this solution. The polymerization was initiated by the addition of several aliquots of 800 µl of 0.03 % hydrogen peroxide added in several small increments. The reactants were stirred for 8 h to complete the polymerization followed by dialysis using Centricon concentrators (10 000 cut-off, Amicon, Inc., Beverly, MA). The samples were then dried under vacuum at 60 °C and used for further analysis.

The gravimetric yield was typically 95 % or higher. A similar procedure was used for the copolymerization, in presence of SPS, of EDOT/PYR (ratio 1:1).

All UV–vis spectra were obtained using a Perkin–Elmer™ Lambda 9 UV–vis/near-IR spectrophotometer. The FTIR measurements were carried out on films cast on ZnSe disk using a Perkin–Elmer FTIR spectrophotometer. Conductivity measurements were performed on pellets using a standard linear four-point probe with a Keithley 619 electrometer/multimeter.

RESULTS AND DISCUSSION

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.

Recently, we reported for the first time, hematin-catalyzed synthesis of the small molecular system and the conjugated bridging ligand, tpphz, and a dinuclear Ru complex [5]. The earlier chemical methods to prepare tpphz used either high reaction temperature (180 °C) or multistep synthesis. One of the most attractive features of our biocatalytic method is the extremely simple synthetic protocol involved. The reaction is a single step and can be carried out under extremely mild and environmentally friendly conditions at room temperature. Using this conjugated bridging ligand, we further synthesized a dinuclear Ru complex with carboxylic acid groups for the DSPV cells.

The UV–vis absorption 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 owing to coupling between aromatic rings. As shown in Fig. 1a, the macrodye spectrum showed a peak at 476 nm, which is due to the metal-to-ligand charge transfer (MLCT). It is indeed interesting to note that the absorption of cut-off wavelength was extended to 800 nm in the polymer. This was an encouraging result from the point of view of efficient light-harvesting in the near-IR region. The UV–vis absorption spectra of the dinuclear complex, Ru-tpphz-Ru is shown in Fig. 1b. The MLCT absorption measured in ethanol solution is 467 nm, which extends up to 600 nm.

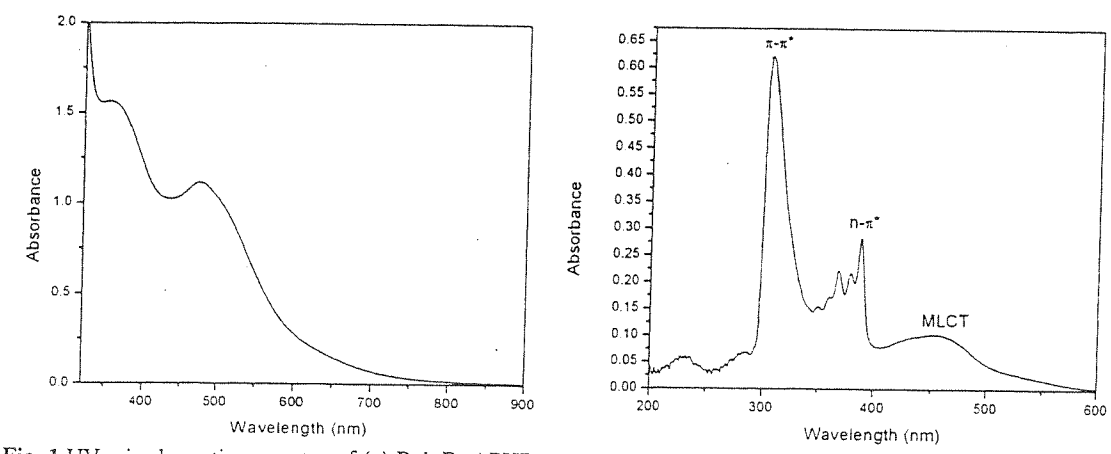


Fig. 1 UV–vis absorption spectra of (a) PolyRuAPHB and (b) Ru-tpphz-Ru.

The photocurrent-voltage curve measured from a sandwich-type dye-sensitized TiO_2 solar cell for the Ru-tpphz-Ru is shown in Fig. 2. The short circuit current density (I_{sc}), open circuit voltage (V_{oc}),

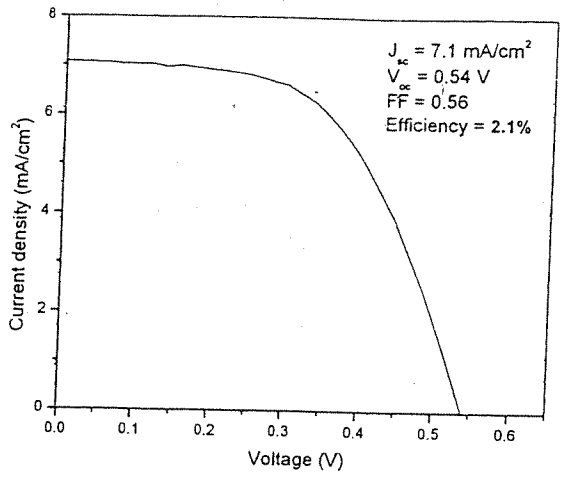


Fig. 2 Current-voltage (I–V) curve for Ru-tpphz-Ru in dye-sensitized solar cell.

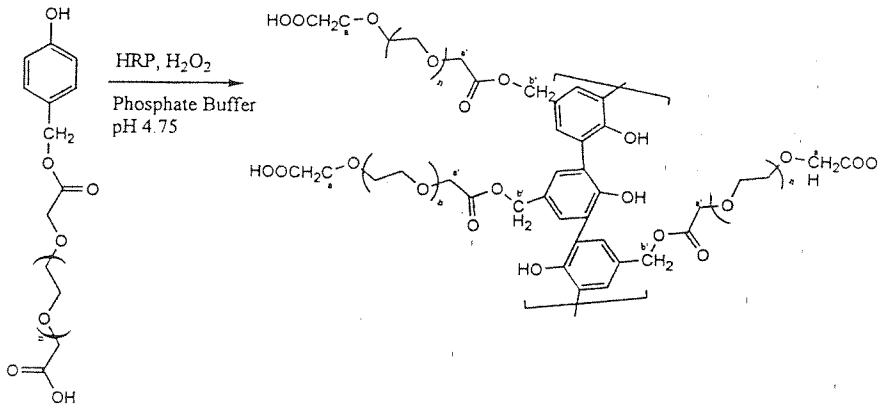
fill factor (ff), and overall efficiency (η_e) for both of the dyes along with the standard dye, N3, are presented in Table 1. The overall efficiency of polyRuAPHB and Ru-tp-Ru dyes in DSPV cells is found to be 0.33 % and 2.1 %, respectively. The dinuclear complex, Ru-tpphz-Ru, is observed to exhibit higher overall efficiency compared to the macrodye, polyRuAPHB. The promising conversion efficiency of these dyes opens up a new class of macrosensitizers and helps in further design of biologically derived macrodyes for the development of molecular solar cells.

Table 1. Short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (ff), and overall efficiency of polyRuAPHB and Ru-tpphz-Ru in TiO_2 dye-sensitized solar cell.

Dye	J_{sc} (mA/cm^2)	V_{oc} (V)	Fill factor	Overall efficiency (%)
PolyRuAPHB	2.10	0.34	0.48	0.33
Ru-tpphz-Ru	7.10	0.54	0.56	2.10
N3	18.75	592	0.43	4.71

Enzymatic polymerization of anilines and phenols leading to conjugated polymers has been reported earlier from work carried out at the University of Massachusetts, Lowell. We have identified some systems that we are currently working on to develop conjugated polymer-based polyelectrolytes based on enzyme-catalyzed polymerization of phenol derivatives. Based on these considerations and our continued interest on the enzymatic synthesis, we have developed the synthesis of pegylated polyphenolics in aqueous media using an environmentally benign catalyst to make the process "green". The schematic representation of HRP-catalyzed polymerization of pegylated phenol macromer is shown in Scheme 3.

The reaction was initially performed in aqueous media at pH 4.75 using phosphate buffer (highest activity of HRP at ~pH 4.75) and was initiated by the increment addition of the H_2O_2 and the product obtained after completion of the reaction was analyzed by its detailed spectral analysis.



Scheme 3 HRP-catalyzed synthesis of pegylated polyphenolics.

The ^{1}H NMR spectrum of the polymer showed broadening of signals as compared to the macromer suggesting the polymerization. The presence of signal at δ 5.0 and δ 4.20 in the polymer spectra was assigned to b' and a', respectively (Fig. 3), confirming the retention of the PEG chains in the polymer.

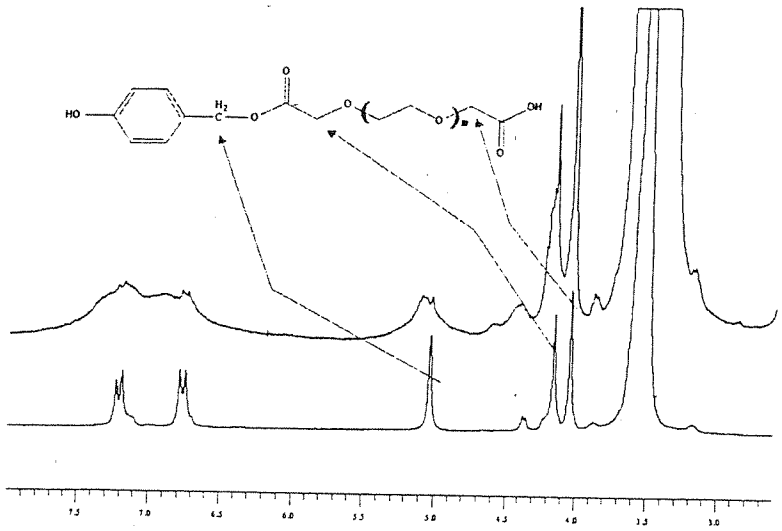


Fig. 3 ^{1}H NMR spectra of the pegylated macromer and polymer.

Figure 4 shows the UV absorption spectra of the pegylated macromer **3** and polymer **4**, with the tailing in the absorption spectra of **4** to 450 nm as compared to **3**. This further confirms the presence of extended conjugation and polymer formation.

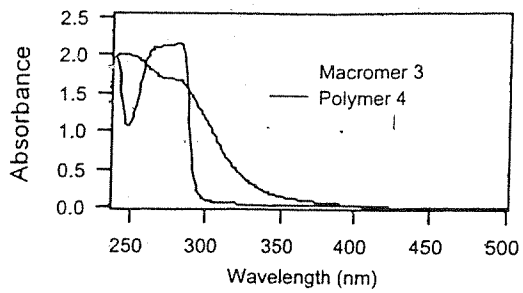


Fig. 4 UV absorption spectra of pegylated macromer **3**, and the pegylated polymer **4**.

We have also studied the effect of pH on the polymerization of the pegylated macromer as shown in Figure 5.

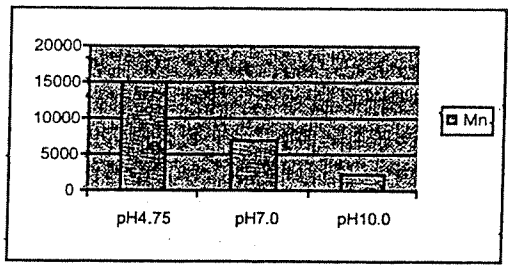


Fig. 5 Effect of pH on the polymerization reactions catalyzed by HRP.

The polymerization reactions were performed at different pH and a decrease in molecular weight of the polymers obtained was observed with the increase in the pH from 4.75 to 10.0. At pH 1.0, no reaction was observed, which is expected as acidic pH, kills the enzyme activity. The highest number average molecular weight (M_n) 15 000 was obtained at pH 4.75, whereas the lowest molecular weight (M_n) 2200 was obtained at pH 10.0. At pH 10.0, we also observed hydrolysis of the ester linkages leading to a mixed polymer where some of the phenyl units were with peg chains and some were not. All of the synthesized polymers were soluble in both organic and aqueous media (except the one obtained at pH 10.0 was soluble only in polar organic solvents like methanol).

The polymerization reaction of EDOT was monitored spectroscopically in an aqueous solution at pH 1.0, and the spectral changes are shown in Fig. 6.

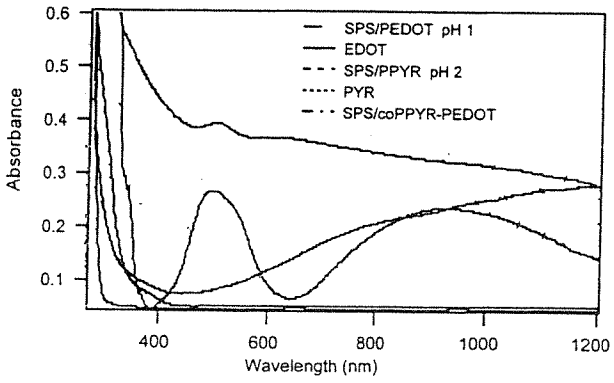


Fig. 6 UV–vis spectra of PYR, EDOT, PEDOT, PPYR, and of co-PPYR-PEDOT.

As seen in the figure, the monomer did not show significant absorption in the range of 380–580 nm. However, initiation of polymerization by the addition of H_2O_2 led to the appearance of absorption from 600 to 1200 nm. This was also accompanied by the change in the color of the reaction solution to a dark blue color with a simultaneous increase in the absorption intensity of the peaks over time. The broad band at 700 nm with a large absorption tail around 1200 nm was attributed to the π-π^* transition in the polymer chain. The FTIR spectrum (Fig. 6) collected after polymerization showed absorption at 1342, 1218, and 976 cm^{-1} all assigned to doping interaction of SPS. The most significant feature, however, was the absence of bands at the range of 1600–1800 cm^{-1}, indicating that no over-oxidation or ring-opening had occurred.

The UV–vis spectrum of the water-soluble SPS/PPYR is shown in Fig. 6. A broad band at 900 nm was assigned to an extended conjugation in the backbone of the PPYR. Moreover, conjugation was also confirmed by the FTIR spectrum of the polymer (Fig. 7), wherein the peaks at 1480/1540 cm^{-1}, assigned to the symmetric and anti-symmetric ring-stretching mode, respectively.

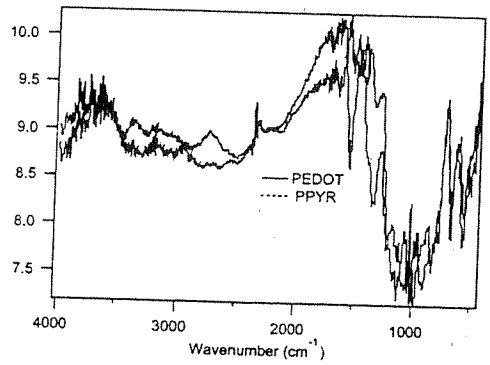


Fig. 7 FTIR of PEDOT and PPYR.

The conductivity data for the PEDOT (1×10^{-5} S/cm) and PPYR (1×10^{-4} S/cm) polymerized with PEG-hematin were determined using the four-point probe. This disappointing result encouraged us to try copolymerization of EDOT with PYR.

The UV–vis spectrum (Fig. 6) of this copolymer showed a large absorbance in the range 400–900 nm while the conductivity measurements of this copolymer were in the range of 0.1–1.0 S/cm. Further investigations are being carried out on these copolymers and are focused on the enhancement of the conductivity and improvement of other physical properties.

CONCLUSION

A new class of Ru complex-based macrodye and a dinuclear complex were synthesized via biocatalytic route employing hematin as an efficient biocatalyst. The MLCT absorption profile of the polymer complex is seen to extend into 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 dinuclear complex was found to be 2.1 % and higher than polymeric complex (0.33 %). However, the promising efficiency observed in these dyes is encouraging from the view of concept of using biocatalytically synthesized macrodyes in photovoltaic cells.

Furthermore, we have developed an environmentally benign methodology for the synthesis of novel pegylated polyphenolics. The reaction conditions used do not require any organic solvents, and all of the reactions were performed in aqueous media. The synthesized polymers were soluble in both organic and aqueous media, and provide further opportunity to tailor the properties.

Finally, a novel biomimetic method for the synthesis of a conducting molecular complex of PPYR and of PEDOT in the presence of a polyelectrolyte, such as SPS is presented. A PEG-modified hematin,

PEG-hematin, was used to catalyze the polymerization of PYR and EDOT in the presence of SPS to form PPYR/SPS and PEDOT/SPS complexes. Copolymers of EDOT and PYR have also been synthesized, and these novel materials have been shown to exhibit high electrical conductivity, with a unique combination of properties such as processability and water-solubility.

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