

## **Tunable heterojunction using conducting polymer for Photovoltaic Application**

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**Abstract :** Developing efficient solar energy capture materials is crucial for the growth of sustainable energy infrastructure in the coming years. Semiconductors used in electronic devices are generally having their fix band properties which are introduced during device fabrication and are not tunable during their application. In current work, it has been demonstrated that it is possible to make heterojunction having variable rectification property even after its fabrication. In-site tunable heterojunction device of the conducting polymers shows variable rectification depending on their band structure. The rectification behavior is studied at various electrochemical potentials and pH. The rectification ratios are extracted from various current densities (J)-voltage (V) plots and correlated with bandgap differences of the constituent polymers. Ideality factors of the device are also extracted from log J-V plots. Due to tunable band structure, the device can absorb multiple wavelengths of solar spectrum leading to improved efficiency of the solar cell.

**Keywords :** in-situtuning•heterojunction•polyaniline•polypyrrole•rectification

### **1. INTRODUCTION**

The main problem in heterojunction research is that how nonconventional semiconducting materials can be used to form a heterojunction where fermi level up of their energies with respect to each other is possible according to band structures. This question has given fundamental approaches to the subject which can go to technological implications in various devices made-up of organic substances like conducting polymers, eg. Solar cell,<sup>[1]</sup> light imiting diode,<sup>[2]</sup>schottky devices<sup>[4],[3]</sup>, Photodetector and field-effect transistors (FET).<sup>[5]</sup> With this concern tuning of the band structure of inorganic as well as organic semiconducting materials have been extensively tried choosing appropriate bandgap materials and by changing their inherent properties by the addition of functional groups and doping processes. Chemically and electrochemically manipulation of properties of the organic polymers (plastics) with easy and cheap processing techniques has made polymer-based materials popular in modern society.<sup>[6]</sup> Bandgap control of  $\pi$ -conjugated systems like conducting polymers has been done by developing new synthetic materials with novel procedures and substitutions on basic skeletons.<sup>[7]</sup> For example, strong effects of electrosynthesis conditions can be seen for 3-alkylthiophene and other 3-substituted monomers where attached groups interactions have an indirect effect to control the long-range order in the polymer which controls the bandgap. The innovative properties of the electronic junctions are gained with the difference in the Fermi levels of their components. Heterojunction madeup of conductive polymers which are analogous to conventional heterojunctions, can be of three types such as Schottky (semiconductor/metal), p-n (p type/n type semiconductor), and pP or nN type (isotype). As shown in previous works the majority of such junctions are madeup of a metal (Schootyjunction )or a p-n junction between p and n type and an organic semiconductor conducting polymers. Due to easy degradation of low work function metals like aluminum and from electrochemical potential differences at the rectifying contact, in Schottky junction that cause diffusion of electrode material into the polymer.<sup>[8]</sup> This shortcoming may be conquered by assembling Schottky junctions in which metal as a current collectorto polymer contacts are ohmic.<sup>[9]</sup> Although n-type organic conducting polymers <sup>[10]</sup> areless poplar than p-type polymers due to their lower stability under room temperature conditions, which results in their reductive behavior and faster degradation. Some other reports of p-n junction of conducting polymers are also there related to polyacetylene doped with donors atom such as lithium,sodium, etc. to fabricate it n-type and doped with acceptors atoms such as Bromine,iodine to fabricate it p-type.<sup>[11]</sup> Thick layer p-n junction of electrochemically synthesized polypyrrole and polythiophene by alkali ion implantation,<sup>[12]</sup> rectifying heterojunction of poly (3,4-dicyanothiophene) and MEH-PPV<sup>[13]</sup> where PDCTh was n-dopable, were

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prepared. Some isotype heterojunctions of conducting polymers were also tried e.g. polymeric heterojunction device consisting of poly(3-octylthiophene) (POT) and PSFT,<sup>[14]</sup> here an alternative approach was applied where two p-type conducting polymers with different bandgaps were engaged to construct an isotype polymeric heterojunction. pP isotype organic heterojunction for ambipolar field-effect transistor<sup>[15]</sup> has been reported in the literature. So pP isotype heterojunctions are advanced then p-n junctions as clear with the description.

Still, whatever is shown above about all type of heterojunctions one thing is common for all that bandgap tuning to become constituents fermi level to form rectifying junction were not in-situ tunable means band structure were determined or fixed during their fabrication and after fabrication of the heterojunctions, their band structures cannot be changed or not changeable in in-situ conditions. The Fermi levels are fixed in all types of heterojunctions. Albeit conducting polymers that can make isotype pP heterojunctions have unique properties that they may have different electrochemical states at different electrochemical potentials. So they possess intrinsically different Fermi levels with these electrochemical states or redox states which are in-situ tunable by changing the electrochemical potential. For the construction of tunable electronic junction the selection of conducting polymer as a semiconductor is tenable since they comprise of various charge carriers (polaron, bipolaron, soliton, and their negative and neutral counterparts) depending upon their electrochemical properties. The energy band diagrams of isotype heterojunction employ the identical expressions and the Fermi level remains constant at thermal equilibrium. Different band gap values by varying the electrochemical potential have been extracted from spectro-electrochemistry of PANI<sup>[6a]</sup> and Ppy.<sup>[16]</sup> Electrochemical conductance of these polymers is prone to their electrochemical states (ECS); moreover, the conductance of polypyrrole and polyaniline can also be tuned by altering the hydrogen ions (pH) concentration. In some cases apparently, the deviation of conductance measured was the magnitude of eight orders within two different electrochemical states, since tuning of the bandgap through electrochemical doping.<sup>[17]</sup> The electrochemical state can be tuned in-situ using a suitable electrochemical technique and this was demonstrated to show in-situ conductance change as a function of the electrochemical state.<sup>[18]</sup> The shifting of the Fermi level controlled by modification in the electronic properties of materials by reduction or oxidation procedure.<sup>[19]</sup> So with the combination of two conductive polymers like PANI and Ppy, it is possible to prepare pP isotype in-situ tunable hetero-junction with variable rectification ratio and junction properties. For in-situ tuning of conducting polymer, the technique involves two electrodes linked utilizing the electroactive polymer. The potential of these two electrodes can be run independently and was used by concerning an identical reference electrode. For fixing of electrochemical states of the polymers, it was required to apply the same potential to both electrodes. The other parameter such as bias voltage and the polarity were regulated by appropriately tuning the potential of each electrode. The methods are shown elsewhere in conductometric sensing with in-situ tuning of the polymers.<sup>[20]</sup> In current set of experiments the technique used as earlier<sup>[20a]</sup> has been applied for developing the tunable hetero-junction. Here we maintained the electrochemical states of the polymers and, to generate current density-voltage (J-V) curve, steps of bias voltage was superimposed over the electrochemical potential. The band structure of the polymers in the device at a particular electrochemical state shown rectification behavior in The J-V curve .

## 2. RESULTS AND DISCUSSION

The device : The device was fabricated using two platinum wires which were attuned together on a Teflon base at 50  $\mu\text{m}$  distance using a mold and seen by SEM. One Pt wire working electrode was named as W1 and the other one as W2 (fabrication steps are shown in Figure 1). Schematic of electropolymerization on custom-made device and SEM images of the heterojunction device is shown in Figure 2. It is clearly shown that sequence is maintained to fabricate the device as Polyaniline over-oxidized at higher potential so Polypyrrole was polymerized first then PANI polymerized on other working electrodes. The junction was prepared in a custom-made device consisted of two platinum wires as shown in Figure 2A(a). Two conducting polymers were grown from either side of the device and Ppy (black color) was first grown as shown in Figure 2A(b) then PANI (green color) was grown on

other platinum wire working electrode and heterojunction is formed which is shown in Figure 2A(c). In SEM images distinguished morphologies in PANI and Ppy are clearly shown in Figure 2B(a) and (b), respectively. Ppy grows in a globular-like morphology and PANI is fibrous-like. These can be differentiated in SEM images of heterojunction in Figure 2B(c), (d), (e) and (f) at different magnifications. Ppy (granular) and PANI (fibrous) are forming pP heterojunction with good contacts with each other. So the intimacy of the contacts can be seen by these SEM images of the heterojunction. A gross view of the heterojunction captured by SEM is given in Figure S1(a) and Figure S1(b) (at higher magnification).

Band structure and J-V plots : Generally all conducting polymers show multiple band structures at various electrochemical states. Like this property, Ppy and PANI also show various band structures with varying electrochemical potential, which can be seen by their spectroelectrochemistry where UV-Vis band shifting is continuously observed with the change of electrochemical potential. As shown in Figure 3(a) PANI and Ppy band gaps are changing with the electrochemical state which shows their neutral and oxidized states at -200 mV and 400 mV potential. Since this property is reversible, it is possible to fabricate an in-situ tunable heterojunction of Ppy-PANI. A schematic representation of band structures under various conditions is given in Figure 3(b) where relative positions of band energies as a function of electrochemical potentials are clearly shown.

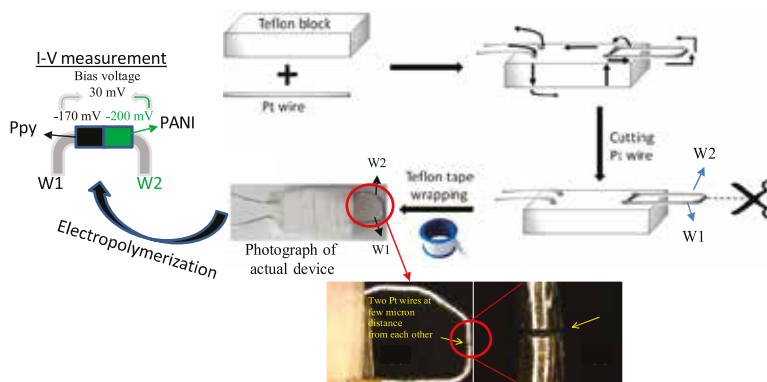


Figure 1: Schematic drawing of the fabrication steps of the device for electropolymerization of conducting polymers on W1 and W2 working electrodes and I-V measurements.

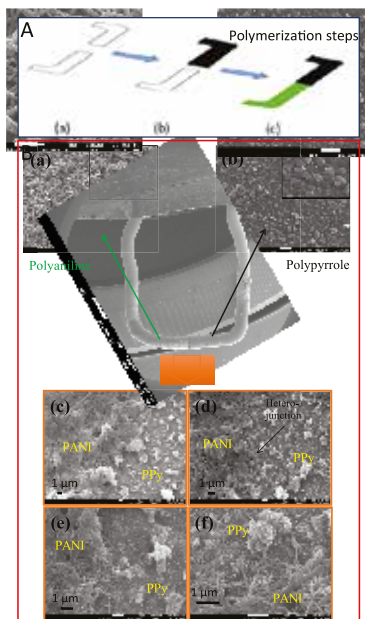


Figure 2 : Schematic of growing polymers on W1 and W2 working electrodes; A(a) Bare platinum electrodes, A(b) Ppy grown on an electrode (black colored), A(c) PANI on the second electrode (green colored); SEM images of conducting polymers grown over Pt wires B(a) PANI, B(b) Ppy; B(c), B(d), B(e) and B(f) SEM images of the heterojunction showing PANI (fibrous structure) and PPy (granular structure) at different magnifications.

Ppy and PANI are considered as p-type and P-type semiconductors respectively which owing low bandgap in case of Ppy and high bandgap in PANI in undoped condition. Here it can be said that the Fermi level for PANI, having a higher bandgap will be at a higher energy level than Ppy which has a comparatively lower bandgap, and therefore the band bending will be towards the Ppy. In this determination, the forward bias is measured when Ppy associated negative polarity and PANI to positive polarity. The J-V plots of Ppy-PANI heterojunction plotted using current density and potential data obtained from experiments at various ECS and pH are shown in Figures 4 and 5. At -200 mV and 0 mV, ECS and pH 1 to 4 related curves are given in Figure 4 and at 200 mV and 400 mV ECS and pH 1 to 4 related curves are given in Figure 5. At -200 mV and 0 mV, ECS plots are more curved than at 200 mV and 0 mV which can be explained by the band structures which are elaborated in detail below. The J-V characteristics show varying rectification behavior corresponding to different bandgap difference values of the polymers. Values of the corresponding rectification ratios (RR) are furnished in Table 1.

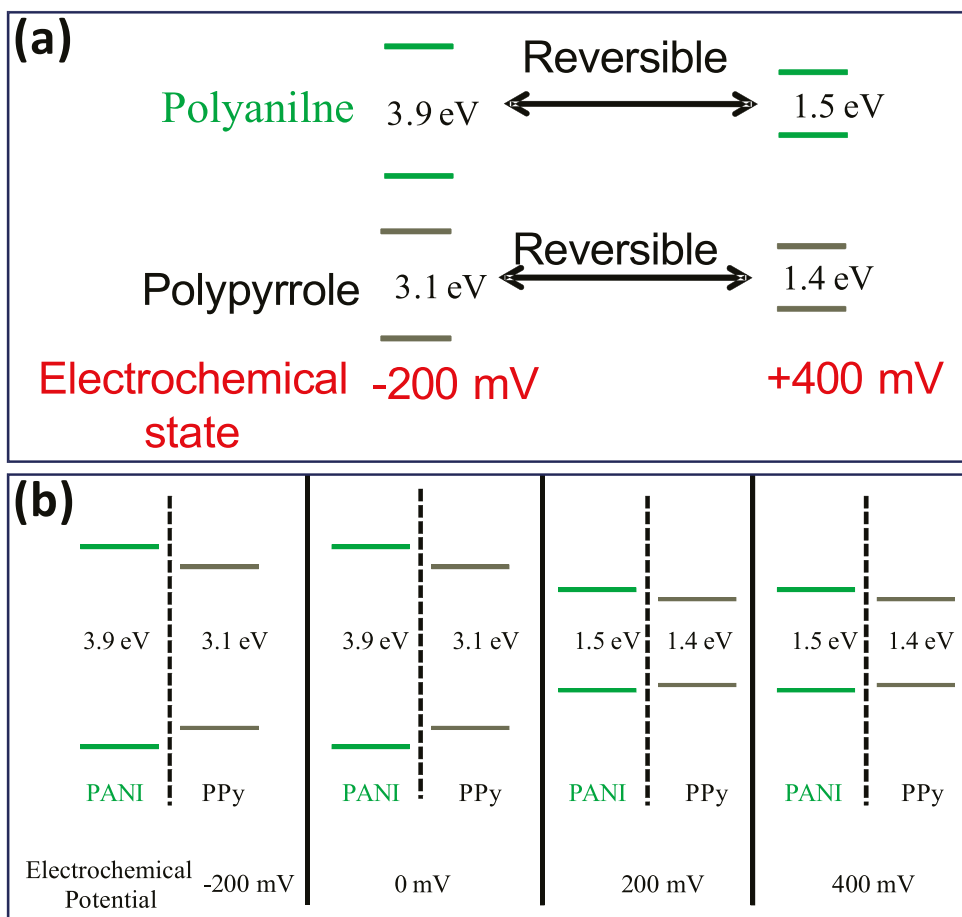


Figure 3. (a) Schematic of showing reversibility in the bandgap of PANI and Ppy at the electrochemical potential of -200 mV and +400 mV; (b) A schematic band diagram showing band gaps of PANI and Ppy at different electrochemical states before contacts

Electrochemical state of the polymers and rectification ratio of the device: As it is already said that band structures (band gaps) are tunable for Ppy and PANI conducting polymers as electrochemical potential changes. At lower electrochemical potentials -200 mV and 0 mV Ppy remains in its neutral form and at higher potential values 200 mV and 400 mV it is in its oxidized form or bipolaronic form.[21] Generally, Ppy shows a series of absorption spectrum in its neutral form in between -0.9 V to 0 V and oxidized forms at higher potentials depending upon the applied potentials. At 0 mV, its state does generally neutral but still, it is a more oxidized state than -200 mV. But here only two different band gap values are considered for neutral and oxidized forms of Ppy. Moving towards the anodic direction, Ppy changes its bandgap values with minute differences which can be observed in obtained

J-V plots and RR values at -200 mV and 0 mV also. Ppy in its neutral state generally shows a bandgap value of 3.1 eV[16, 21] This value is reported in the literature and assigned to  $\pi \rightarrow \pi^*$  transition of the neutral pyrrole monomer. As we go anodic ( $> 0$  mV) it gets converted into oxidized form gradually and at 200 mV and 400 mV corresponding bandgap get decreased to 1.4 eV.[21] Due to the presence of neutral state and polaron/bipolaron same type of variations in bandgap values at different potentials are also reported for PANI. At -200 mV potential polyaniline shows its neutral leucoemeraldine ( $\pi \rightarrow \pi^*$  transition) form and its band gap has been reported to be 3.9 eV[6a, 22] which is higher than Ppy at the same potential. This leucoemeraldine form gets converted into protoemeraldine form at 0 mV potential then converts into emeraldine form at about 150 mV and is characterized by half oxidized form of PANI. So like Ppy, gradual change in electrochemical states is also observed for PANI. [20a] This emeraldine form shows an intermediate polaron band with a bandgap value of 1.5 eV.[6a] At additional anodic potential PANI gets changed into a fully oxidized form, the pernigraniline with a band gap of 2.2 eV, though this form of PANI is exceeding the range of current study. Schematic diagrams showing relative positions of band energies as a function of electrochemical potentials are already specified in Figure 3. So in the present work, we have considered two-band gap values for each polymer at different electrochemical potentials.

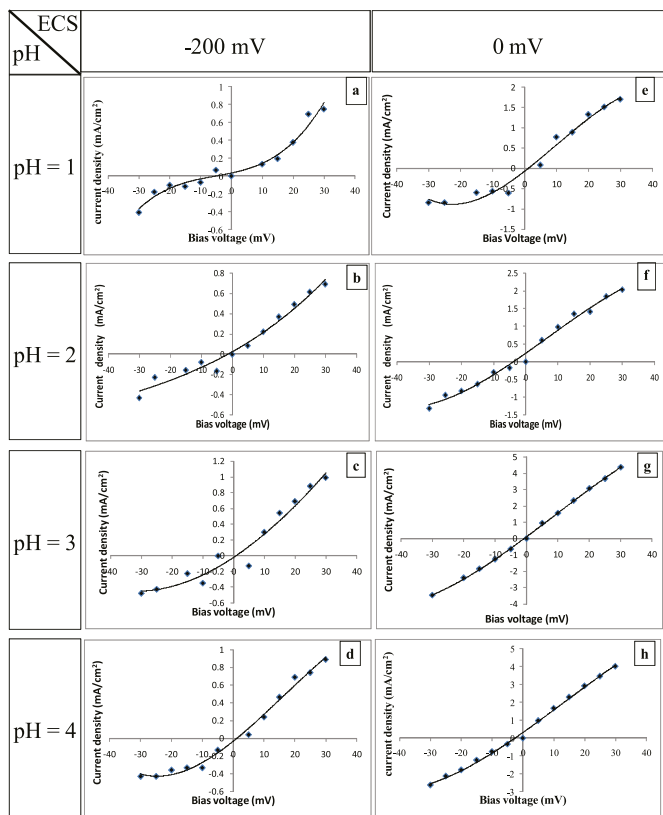


Figure 4. J-V plots of Ppy-PANI junction in different conditions. (ECS -200 mV and 0 mV; pH 1 to 4)

A significant variation can be observed in the J-V plots of the Ppy-PANI heterojunction due to the varying band structure of Ppy and PANI. On comparing the rectification ratio and shape of the obtained J-v Curves at -200mV. (Figure 4a-d), it may be observed that the shape are almost similar and almost the same values of rectification ratios were obtained by calculation for all pHs as shown in Table 1. This is because Ppy and PANI neutral forms at this potential due to the inability to generate charge carriers (polaron), here no effecto pH was found on rectification ratio at -200mV potential. The somewhat higher value of RR at pH 1 than other pHs is due to a better combination at higher proton concentration in the electrolyte. The J-V curves at 0 mV (Figure 4e-h) have the same type of shape as observed at -200 mV but the RR values for these are lesser. The  $\Delta$ (bandgap) value and rectification ratio are plotted as a function of ECP in Figure 6. Also at 0 mV and pH, 1 RR value is similar to the

value at -200 mV and which is decreasing with increasing. At all other combinations of pHs and potentials curve shapes are getting linear gradually so RR values are also decreasing and reaching 1 as can be seen in Figure 5. The highest rectification ratio (2.52) at -200 mV than other potentials has been observed due to the highest difference in the band gap of PANI and Ppy.

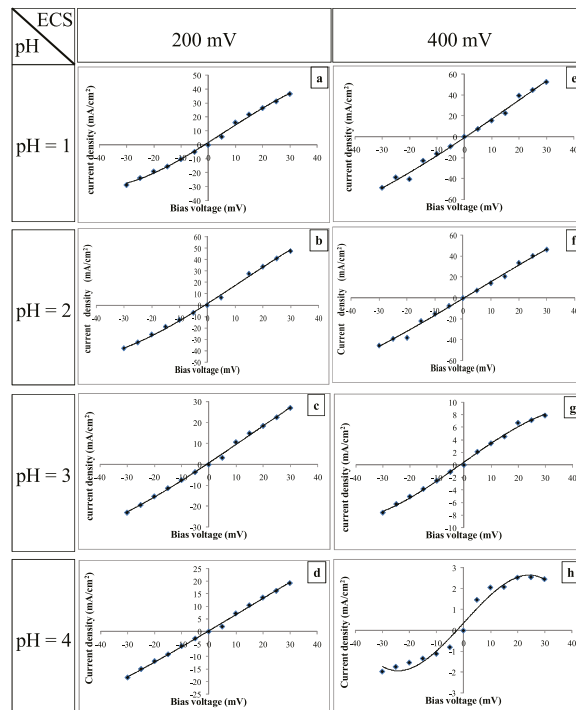


Figure 5. J-V plots of Ppy-PANI junction in different conditions. (ECS 200 mV and 400mV; pH 1 to 4)

At +200 mV and +400, mV potential band gap values for both the polymers become almost similar and a negligible bandgap difference has been observed. So here we get linear J-V plots in all pHs (Figure 5a-h). Ohmic behavior has been observed in these cases where the  $\Delta$  (bandgap) is around zero and no rectification is observed. The  $\Delta$  (bandgap) value and rectification ratio are plotted as a function of electrochemical potential for Ppy-PANI junction as shown in Figure 6. A direct relationship A direct between the value of  $\Delta$  (bandgap) value and RR values can be seen in Figure 6 at all pHs.

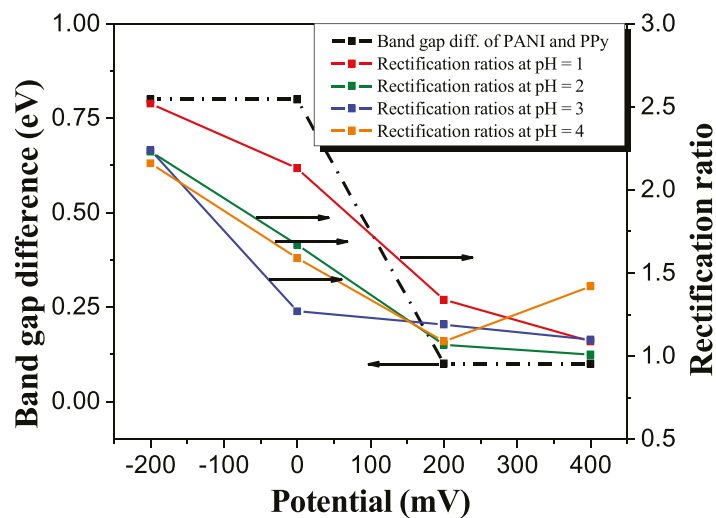


Figure 6. Plots of change in rectification ratios with electrochemical potentials of Ppy-PANI heterojunction according to constituent polymers  $\Delta$ (bandgap) or band structures.

Effect of pH on rectification ratio : The conductance of both the polymers is dependent on pH and it is inter-convertible from conductive to insulator regime from lower pH to higher pH. For both the polymers in-situ conductivity increases by a factor of  $10^4 - 10^5$  by changing pH from 7 to 0.8.<sup>[23]</sup> As shown in literature for Ppy, resistance increases significantly as we move from lower to higher pH. Concerning the fact that protons are involved in the charge transfer process during in-situ measurements. During the proton doping process, Ppy amine units (at cathodic potentials) convert into the Ppy imine units (at anodic potentials) with the change of bandgap from around 3.1 eV to 1.4 eV.<sup>[24]</sup> This change in conductivity is also observed in J-V plots where at higher ECS current response is higher than lower ECS (Figure 4 and 5). Also, it is notable that at 200 mV and 400 mV ECS by increasing pH, the current response is decreasing as shown in Figure 5. Polyaniline shows metal-to-insulator transition from pH 1 to pH 4.<sup>[25]</sup> The proton doping converts benzenoid amine nitrogen units to quinoid imine nitrogen units to a semiquinone nitrogen cation type polaronic lattice. This distortion of lattice in amine nitrogen results in a polaronic band having a bandgap of 1.5 eV. Therefore, after protonation at anodic potentials onwards to 200 mV, the bandgap of unprotonated polyaniline decreases from 2.1 eV to 1.5 eV.<sup>[6a]</sup> Although the band structure does not change much in pH lower than 4 for PANI. According to previous reports of cyclic voltammogrammic and infrared spectroscopic recordings it was explained that the conductance was absent of PANI at pH > 4.<sup>[26]</sup> We therefore restricted our study till pH 4. Further very little protonation is reported in the leucoemeraldine form of PANI. So conductivity also affect the shape of obtained J-V curves. These variations in the shape of J-V plots (Figure 3 and 4) and the rectification ratio (Table 1) have been observed with changing

**Table 1: Band gap differences and rectification ratio of Ppy-PANI heterojunction at different electrochemical potentials from pH 1 to pH 4.**

Electrochemical Potential (mV)	PANI Band Gap (eV)	Ppy Band Gap (eV)	Band gap diff. (eV)	Rectification ratio at pH = 1	Rectification ratio at pH = 2	Rectification ratio at pH = 3	Rectification ratio at pH = 4
-200	3.9	3.1	0.8	2.52	2.23	2.24	2.16
0	3.9	3.1	0.8	2.13	1.67	1.27	1.59
200	1.5	1.4	0.1	1.34	1.07	1.19	1.09
400	1.5	1.4	0.1	1.09	1.01	1.10	1.42

the pH. Significant rectification has been observed at pH 1 and 2 in less-doped polymers with a decrement with increasing pH. In the case of -200 mV ECS very close RR values are obtained at all pHs it means here RR is governed by ECS only. Whereas at 0 mV ECS, it is governed by pH and ECS. At 200 mV and 400 mV, the J-V curves found close to linear and at these anodic potentials, the rectification is not controlled by the PH, however it is mostly controlled by the ECS.

**An Ideality factor :** The representative Log J-V plots of the heterojunction recorded at various ECS and pH 3 are given in Figure 7. The ideality factors have been calculated from the linear portion of the Log J-V plots.<sup>[20a, 27]</sup> The values of the calculated ideality factors are given in Table 2. In ideal conditions, the ideality factor is generally said to be 1. The derivation of the simple diode equation uses certain assumptions about the cell or device. Typical values of ideality factor of a diode are generally in between 1 and 2 or it can be greater or lower, this may be due to recombination of charge carriers in different ways in the devices which in results does not follow the simple diode equation. Albeit in the present case we obtained ideality factor values less than one as shown in Table 2. The lower value of the ideality factor may be contributing to the low biasing voltage and availability of fewer charge carriers for recombination in conducting polymers as reported in the literature.<sup>[20a]</sup> Log J-V plots in all conditions are given in Figures S2 and S3.

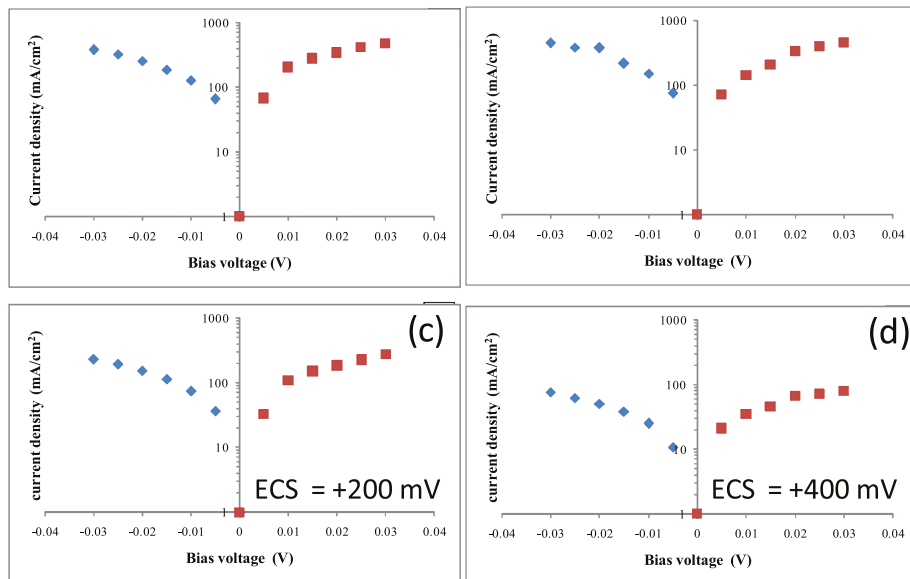


Figure 7. Representative log J-V plots of Ppy-PANI heterojunction in pH = 3 at (a) -200 mV (b) 0 mV (c) 200 mV and (d) 400 mV.

**Table 2 : Ideality factor of Ppy-PANI heterojunction at four different electrochemical potentials. Ideality factors are shown in pH 1 to pH 4 buffer solutions.**

Electrochemical Potential (mV)	Ideality Factor			
	pH = 1	pH = 2	pH = 3	pH = 4
-200	0.78	0.86	0.94	0.93
0	0.82	0.85	0.65	0.71
200	0.61	0.56	0.52	0.48
400	0.59	0.52	0.53	0.87

### 3. CONCLUSIONS

Conducting polymers could be promising candidates to make electronic devices where the in-situ tuning of rectification behavior at the heterojunction is needed for specific purposes. In current work, in-situ tuning is demonstrated having the example of semiconductors Ppy and PANI. These polymers have a tunable bandgap as a function of their electrochemical states and this property is used to fabricate in-situ tunable pP heterojunction. The heterojunction was studied at -200 mV, 0 mV, 200 mV, and 400 mV electrochemical potentials and the highest rectification ratio was obtained at -200 mV and at pH1, where the band gap difference of both the polymers was highest. In this study obtained ideality factors are less than one due to fewer charge carrier recombinations in the conducting polymers. This fundamental approach opens doors for new possibilities in practical applications in electronics.

### 4. EXPERIMENTAL SECTION

**Required chemicals and device fabrication :** Pyrrole and Aniline were purchased from Sigma-Aldrich. Both were doubly distilled and stored at low temperatures under an inert atmosphere. AR grade sulphuric acid (s.d. fine. chem.) was used as an electrolyte for the polymerization of monomers. Salts of analytical gradewere used for the preparation of pH buffers without further purification. 0.1 M Aniline and 0.1 M Pyrrole monomer solutions



were prepared in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution separately. Milli-Q water (0.5 μS<sub>cm</sub><sup>-1</sup>) was used to prepare all solutions. Device assembly was prepared like our previous work.<sup>[20a]</sup> in which two working electrodes were fabricated using the Platinum wire (99.9%, metal basis) of 0.5 mm diameter. Platinum foil and Ag/AgCl (sat. KCl) were used as reference and counter electrodes respectively. Platinum wires working electrodes assembly connected to Pine bi-potentiostat (AFCBP1) was used to conduct all electrochemical experiments at room temperature.

Fabrication steps are already shown in Figure 1. All electrodes were properly washed with water and acetone and tested electrochemically for any impurity. Since Polypyrrole polymerizes at potential anodic to Polyaniline, it was polymerized first on W1 platinum wire. Potentiostatically, the electrode was working at 1.2 V vs Ag/AgCl (sat KCl) for 10 minutes. After polymerization of Ppy device assembly was washed with milli-Q water to remove Pyrrole monomer from the electrode surface and dried for 2 hours at room temperature. It was ensured that both W1 and W2 working electrodes are not been connected only by Ppy with the help of a multimeter. Now polyaniline was coated on the W2 electrode to form a bridge with pre-deposited Ppy for which a heterojunction was formed. Now the device was again washed and dried. The Ppy-PANI heterojunction morphology was seen by scanning electron microscope SEM (model JEOL JSM 7100F) at an acceleration voltage of 15 kV. The SEM sample was an entire heterojunction device coated with Au-Pd alloy with a sputter cotter, placed on a sample holder.

**I-V measurements** : I-V measurements were done according to our previous work.<sup>[20a]</sup> Device and electrode connected to their respective terminals to bi-potentiostat were set in a compartment in a 10 mL buffer solution. The conductometric measurements were done at pH 1 to pH 4 buffer solutions and at -200 mV, 0 mV, 200 mV, and 400 mV electrochemical potentials. Using bi-potentiostat the in-situ current was measured. To measure the current-voltage characteristics, a voltage window of ±30mV was considered. For example to ensure that the electrochemical potential remains -200 mV, one working electrode (W2) was operating on a fixed potential -200 mV and the bias voltage was altered by varying the potential of the working electrodes (W1) from -170 mV (forward bias) to -230 mV (reverse bias) as shown in Figure 1. The applied bias voltage was varied from -30mV to +30mV a step of 5 mV potential window. The voltage window was kept small to maintain the electrochemical states of the Polypyrrole and Polyaniline. The current of the working electrodes was measured in both zero bias and biased conditions and the background current measured at zero bias (when the same potential was maintained for both W1 and W2 electrodes) condition was under study from the current of the device. The current densities (J) were calculated by normalizing the obtained current in each experiment through division by the cross-sectional area of the device and used for plotting J-V and Log J-V plots. Bias voltage and Current (passed through junction) values were extracted from subtracting the applied potential values and obtained current values of W1 and W2 electrodes respectively.

## 5. ACKNOWLEDGMENTS

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## 6. REFERENCES

- [1] S. Guenes, H. Neugebauer, N. S. Sariciftci, Chem. Rev. (Washington, DC, U. S.), 107, 1324-1338, 2007.
- [2] J. Shi, S. Zheng, Macromolecules, 34, 6571-6576, 2001.
- [3] T. Barman, A. R. Pal, ACS Appl. Mater. Interfaces, 7, 2166-2170, 2015.
- [4] R. Rivera, N. J. Pinto, Phys. E (Amsterdam, Neth.), 41, 423-426, 2009.
- [5] F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, Science (Washington, D. C.), 265, 1864-1866, 1994.
- [6] W. S. Huang, A. G. MacDiarmid, Polymer, 34, 1833-1845, 1993; b) H. Spanggaard, F. C. Krebs, Sol. Energy Mater. Sol. Cells, 83, 125-146, 2004.

- [7] J. Roncali, Chem. Rev. (Washington, D. C.) 97, 173-205, 1997.
- [8] E. Gautier, A. Lorin, J.-M. Nunai, A. Schalchi, J.-J. Benattar, D. Vital, Appl. Phys. Lett., 69, 1071-1073, 1996.
- [9] A. N. Chowdhury, Y. Harima, Y. Kunugi, K. Yamashita, Electrochim. 41, 1993-1997, Acta 1996.
- [10] A. G. Manoj, K. S. Narayan, Opt. Mater. (Amsterdam, Neth.) 21, 417-420, 2003.
- [11] C. K. Chiang, S. C. Gau, C. R. Fincher, Jr., Y. W. Park, A. G. MacDiarmid, Univ. Pennsylvania, p. 18 pp, 1978.
- [12] B. Lucas, B. Ratier, A. Moliton, J. P. Moliton, T. F. Otero, C. Santamaria, E. Angulo, J. Rodriguez, Synth. Met. 55, 1459-1464, 1993.
- [13] Y. Greenwald, X. Xu, M. Fourmigue, G. Srdanov, C. Koss, F. Wudl, A. J. Heeger, J. Polym. Sci., Part A: Polym. Chem. 36, 3115-3120, 1998.
- [14] T.-T. Ong, S.-C. Ng, H. S. O. Chan, R. V. Vardhanan, K. Kumura, Y. Mazaki, K. Kobayashi, J. Mater. Chem. 13, 2185-2188, 2003.
- [15] (a) H. Wang, X. Wang, B. Yu, Y. Geng, D. Yan, Appl. Phys. Lett. 93, 113303/113301-113303/113303, 2008; (b) X. Guo, F. Hong, W. Jin, W. Gu, H. Zhang, J. Wang, Org. Electron, 11, 876-880, 2010.
- [16] P. Rapta, A. Neudeck, A. Petr, L. Dunsch, J. Chem. Soc., Faraday Trans. 94, 3625-3630, 1998.
- [17] E. W. Paul, A. J. Ricco, M. S. Wrighton, J. Phys. Chem. 89, 1441-1447, 1985.
- [18] (a) P. G. Pickup, R. W. Murray, J. Electrochem. Soc. 131, 833-839, 1984; (b) D. Ofer, R. M. Crooks, M. S. Wrighton, J. Am. Chem. Soc. 112, 7869-7879, 1990.
- [19] H. Koezuka, K. Hyodo, A. G. MacDiarmid, J. Appl. Phys. 58, 1279-1284, 1985.
- [20] a) R. Gupta, A. Paul, J. C. Chaudhari, D. N. Srivastava, Synth. Met. 220, 95-101, 2016; b) M. Kanungo, D. N. Srivastava, A. Kumar, A. Q. Contractor, Chem. Commun. (Cambridge, U. K.) 680-681, 2002; c) A. K. Ajay, D. N. Srivastava, Biosens. Bioelectron. 23, 281-284, 2007.; d) C. Muthukumar, S. D. Kesarkar, D. N. Srivastava, J. Electroanal. Chem. 602, 172-180, 2007; e) A. Paul, M. Perween, S. Saha, D. N. Srivastava, A. Das, Physical Chemistry Chemical Physics 2015, 17, 26790-26796, 2015.
- [21] T. Amemiya, K. Hashimoto, A. Fujishima, K. Itoh, J. Electrochem. Soc. 138, 2845-2850, 1991.
- [22] A. Malinauskas, R. Holze, Synth. Met. 97, 31-36, 1998.
- [23] J. Lippe, R. Holze, Molecular Crystals and Liquid Crystals 1991, 208, 99-108, 1991.
- [24] A. P. Bonifas, R. L. McCreery, Analytical Chemistry, 84, 2459-2465, 2012.
- [25] A. J. Epstein, J. M. Ginder, F. Zuo, R. W. Bigelow, H. S. Woo, D. B. Tanner, A. F. Richter, W. S. Huang, A. G. MacDiarmid, Synth. Met. 18, 303-309, 1987.
- [26] a) H. Neugebauer, A. Neckel, N. S. Sariciftci, H. Kuzmany, Synth. Met. 29, E185-E192, 1989, b) W. E. Rudzinski, L. Lozano, M. Walker, J. Electrochem. Soc. 137, 3132-3136, 1990.
- [27] R. Singh, D. N. Srivastava, R. A. Singh, Synth. Met., 121, 1439-1440, (2001).