

Rectifying Characteristics of Metal Organic Junction Diodes Based on a Porphyrin and Its Diprotonated Analogue

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Abstract

We have demonstrated the rectifying properties of metal/organic junction diodes based on a simple porphyrin and its diprotonated version. *Meso*-tetraphenylporphyrin (H_2TPP) and its diprotonated version were spin-coated separately on the surface of copper (Cu) to produce thin films. Current-voltage characteristics revealed that rectifying capacity of Cu/ H_2TPP junction is poor. However, metal/organic junction diode in the thin film of the diprotonated form of H_2TPP exhibited excellent rectification upon structural modification induced by protonation of the two nitrogens in the porphyrin core

Keywords

Organic semiconductor; Rectifying diode, Tetraphenylporphyrin, Metal-organic junction, Diprotonation

1. Introduction

Rectifying diodes are important parts of the electronic circuits present in all electronic equipment and their function is to convert alternating current (AC) to direct current (DC) [1]. Nowadays, inorganic semiconductor elements (mainly silicon) make up over 90% of rectifying diodes used in electronics [2]. Simple organic molecule-based rectifying diodes have garnered a lot of attention recently due to their many benefits, including affordability, adaptability, soft processing, and environmental friendliness [2]. Rectifying diodes based on organic semiconductor molecules have been reported, however most of the time the molecules are not easily synthesizable [3]. Long conjugated π electrons in organic semiconductors were projected to have potential for usage as rectifying diodes. However, compared to inorganic semiconductors, organic semiconductors also have certain drawbacks, such as higher resistance, shorter lifespans, and a greater reliance on stable environmental conditions [4]. An important class of macrocycles with 22 conjugated π electrons, porphyrins are regarded as excellent organic semiconductors. Structure and electronic properties of the porphyrins can be modulated by various ways such as metallation, substitution, protonation, oxidation *etc* [5]. Several researches have been conducted to understand the impact of porphyrin structure modulation on its electronic

and spectroscopic properties [5]. To the best of our knowledge no research has been done on how protonation-induced structural modification in porphyrin affects diode rectification features. *Meso*-tetraphenylporphyrin (H_2TPP) is easy to synthesize and it is highly stable [6]. In order to understand the impact of the structural modification resulting from the protonation of porphyrin on rectifying capabilities, we report here the I-V characteristic features of the metal/organic junctions in the thin films of H_2TPP and its diprotonated version, $[H_4TPP]^{2+}$.

2. Experimental Section

H_2TPP was synthesized by published method [6]. Trifluoroacetic acid (TFA) was used to protonate H_2TPP to produce dark green $[H_4TPP]^{2+}$ [7]. Structures of the two compounds are shown in Fig. 1. Thin films of H_2TPP and $[H_4TPP]^{2+}$ were prepared using a spin coater. Each compound was dissolved in chloroform and approximately 1 mL saturated solution was added on a piece of thin copper plate kept inside the chamber of spin coater. The plate was immediately rotated at 3000 rpm for 10 seconds. The resulting thin films were vacuum-dried for a further thirty minutes without being rotated. We have measured I-V characteristics of the devices using Keithley 2401 source meter. The

point-by-point I-V characteristics were recorded, with a 2 minute gap between each measurement.

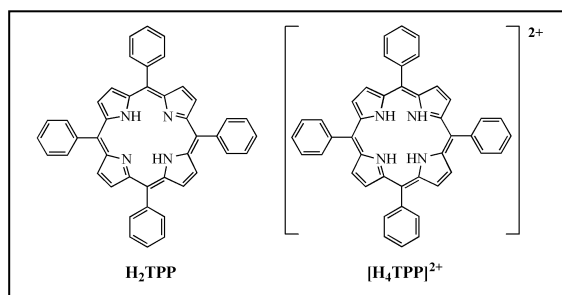


Fig. 1. Structure of the organic semiconductors used in the study

3. Results and discussion

Conversion of H₂TPP to [H₄TPP]²⁺ by protonation was studied by UV-vis spectroscopy. A solution of H₂TPP (10⁻⁶ M) in chloroform was titrated with drop wise addition of diluted solution of TFA in chloroform. UV-vis spectra were recorded after each addition. Time evolution UV-vis spectra are shown in Fig. 2. No spectral change after addition of 2 equivalent of TFA with respect to H₂TPP indicated diprotonation of the two nitrogen atoms present in the core of H₂TPP. Earlier studies also revealed that protonation of H₂TPP by excess TFA form the diprotonated analogue [H₄TPP]²⁺ exclusively. Characterization and detailed structure analysis of [H₄TPP]²⁺ have already been published elsewhere [7]. Spectral change associated with 4 clear isobestic points in the UV-vis profile (Fig. 2) indicates clean conversion of H₂TPP to [H₄TPP]²⁺. UV-vis spectra of the [H₄TPP]²⁺ solution in chloroform and other organic solvents remained unchanged even after being stored for two weeks or more in normal atmospheric condition. This demonstrated the compound's high stability and robustness.

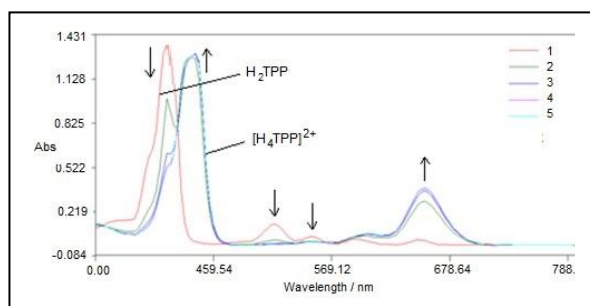


Fig. 2. Time evolution UV-vis spectra demonstrating conversion of H₂TPP to [H₄TPP]²⁺ by successive addition of TFA into a solution of H₂TPP in chloroform.

Thin films of H₂TPP and [H₄TPP]²⁺ were prepared according to the procedure mentioned in the experimental section. I-V characteristics of the metal/organic junction diodes were studied using the thin films and the resultant plots are shown in Fig. 3. In this work we have compared the diode characteristics between two junctions, Cu/H₂TPP and Cu/[H₄TPP]²⁺. Fig. 3 shows that for the Cu/H₂TPP junction-based structure, the reverse bias current is rather significant, indicating that this structure has poor rectifying behaviour. However, the Cu/[H₄TPP]²⁺ junction-based structure exhibits a negligible current on reverse bias, which is an essential condition for rectifying diodes.

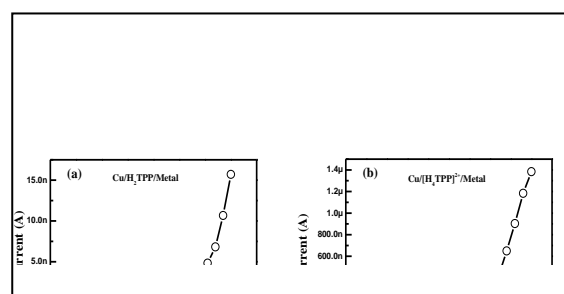


Fig. 3. I-V characteristic features of the metal/organic junction diodes Cu/H₂TPP/Metal (left) and Cu/[H₄TPP]²⁺/Metal (right)

Our devices show Schottky diode behaviour. Forward bias (positive voltage) reduces the Fermi energy of Cu relative to the porphyrin (H₂TPP or [H₄TPP]²⁺). As a consequence, the potential drop across the porphyrin is reduced. Hence, the equilibrium between diffusion and drift is altered, with more electrons diffusing in the direction of Cu than drifting toward the porphyrin. Consequently, a positive current passes through the Cu/porphyrin junction. In comparison to the Fermi energy in the porphyrin, the Fermi energy of Cu increases when reverse bias, or negative voltage is applied. This results in a larger depletion region and an increased electric field at the interface as the potential across the porphyrin rises. In this way, flow of electrons now becomes limited. This implies that a significant amount of current flows across the Cu/porphyrin junction when the bias is forward, whereas, essentially no current flows when the bias is reversed.

It is well established that protonation of porphyrins at the core nitrogens makes them non-planar. Diprotonation of porphyrins results even more non-planarity [5]. The π - π^* energy gap in non-planar porphyrin is lower compare to that of similar planar porphyrin because energy of the HOMO increases with increase in non-planarity, whereas, energy of the LUMO remains almost unaffected [8]. Therefore, decrease in the HOMO-

LUMO energy gap in the $[\text{H}_4\text{TPP}]^{2+}$ compared to that of the H_2TPP is responsible for high rectifying capacity of the $\text{Cu}/[\text{H}_4\text{TPP}]^{2+}$ junction than that of the $\text{Cu}/\text{H}_2\text{TPP}$ junction.

4. Conclusion

Thin films of H_2TPP and $[\text{H}_4\text{TPP}]^{2+}$ were prepared separately on the surface of Cu and rectifying behaviour of these metal-organic junction diodes was studied. I-V characteristic studies revealed that rectifying capacity of $\text{Cu}/\text{H}_2\text{TPP}$ junction is poor. However, $\text{Cu}/[\text{H}_4\text{TPP}]^{2+}$ junction exhibited high rectifying capacity. The outcome of this study demonstrated how protonation-induced structural modification of a simple organic semiconductor enhanced its rectifying performance. To determine the rectifying ratio and comprehend the detailed mechanism of rectification, more research is being conducted.

References

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