Synthesis Of Photosensitizing Polyimide Of Complex Between 3-(2'-Thiazolylazo)- 2,6 - Diamino Pyridine And Ruthenium (II).

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Abstract:
2-aminothiazole was diazotized with sodium nitrite and 6 (M) hydrochloric acid then diazonium salt was coupled with 2,6 - diamino pyridine at 0^0c. Then the solution was basified with 0.001(M) sodium hydroxide solution until P^H=6.0 was reached. A red Precipitate began to settle immediately. Ruthenium (II) complex was synthesized by treating azo dye, 3-(2'-thizolylazo)-2,6-diamine pyridine and dichloro (p-cymene) ruthenium (II)dimer in dry DMF heated at 60^0c for 4h under argon in the dark. Subsequently 2,2'- bipyridine-4,4'-dimethyl was added and the reaction mixture was heated at 140^0c for another 4h. To the resulting solution was added ammonium thio cyanate in water and the reaction mixture was further heated at 150^0c for 3h. DMF was removed on rotary evaporator under high vacuum and water was added to get the precipitate. Polyimide was synthesized by treating ruthenium (II) complex with 6 FDA in presence of DMF firstly stirred at 40^0c for 24h to get viscous polyamic acid then to this solution acetic anhydride and pyridine were added and stirring was continued at 100^0c for 24h.

Keywords :
3-(2'- thiazolylazo) -2,6- diamino pyridine , ruthenium complex, polyimide.

1. Introduction :

Dye sensitized solar cells (DSSCs) have attracted increasing attention as promising alternatives to conventional silicon based solar cells due to their low cost and ease of fabrication . The optimum efficiency of a DSSC device depends upon several parameters and particularly the structure of the sensitizer plays a major role. The ground and excited state energy levels of the dye should be well matched with the highest occupied molecular orbital (HOMO) level of the redox mediator and the conduction band of the semiconductor, respectively, in order to facilitate easy regeneration of the sensitizer and facile electron injection onto TiO_2. Among a large variety of dyes investigated for DSSC application, Ru-sensitizers have attracted more attention because of their low-lying metal-ligand charge transfer (MLCT) transition that extends into the red and near- infrared region of the solar spectrum. In this context much attention has been devoted to enhance the performance of DSSCs by engineering sensitizers.

Dye sensitized solar cells (DSSCs) are fast becoming potential alternatives for the conventional solar cells. The immense attention received by DSSC can be attributed to its cost- efficiency ratio, transparency, flexibility, ecofriendliness and facile chemical modifications. Typically, a DSSC consists of four components, namely a mesoporous nanocrystalline semiconductor, an organic or organometallic dye, an electrolyte and a counter electrode. Each component is very crucial in ensuring the overall efficiency of the cell. However, dye/sensitizer is the most important component of operational DSSC. Until now, the maximum efficiency of 11% has been achieved by a DSSC, fabricated using metal-

based dyes. But the use of noble metals, tedious and laborious synthesis as well as purification steps involved may impede their viability for large scale applications. Therefore, the metal-free organic dyes are of great interest, considering their facile molecular engineering and stronger light-harvesting capability then metal complexes. Further, owing to their high molar extinction coefficient and being comparatively economical, such sensitizers are highly desirable.

Photosensitizer plays an important role in light-harvesting as well as initiating the electrochemical processes for electricity generation. Till now Ru(II) complexes are exploited as excellent photosensitizer in the construction of DSSCs, due to their good photophysical and electrochemical properties. Certain limitations such as use of rare noble metals, availability, manufacturing cost, environmental hazard and problems associated with purification have restricted their further development. On the other hand metal-free organic dyes posess several advantages over the former class, like easy availability, design versatility, high molar extinction coefficients and cost effectiveness in their synthesis. However, the major drawbacks of metal-free dyes in comparison of Ru-complex dyes include their low photovoltaic performance due to the lack of metal-ligand charge transfer (MLCT) bands and their narrow absorption profiles.

2. Experimental :

2.1. Synthesis of 3-(2'-thiazolylazo)-2,6-diamino pyridine :

1.0g of 2-amino thiazole was dissolved in 16 ml of 6 (M) hydrochloric acid and cooled in an ice-bath. Sodium nitrite (0.70g) was dissolved in a small amount of water. After crushed ice was added to both solutions, the nitrite solution was slowly poured into the 2-amino thiazole solution while stirring with a glass rod under low temperature (0^0c). The solution of diazonium salt was slowly poured while stirring into a well cooled solution of 2, 6- diamino pyridine (1.0g) in 40 ml of 4(M) hydrochloric acid. The mixture was stirred in the ice-bath for 1h and then 0.001 (M) sodium hydroxide solution was added into the solution until P^H=6.0 was reached. A red precipitate began to settle immediately. The solution was filtered and the precipitate was washed with water and air dried. The crude product was purified by recrystallization with a mixture of ethanol/water (3:1) to give red needle shaped crystals.

2.2. Synthesis of ruthenium complex :

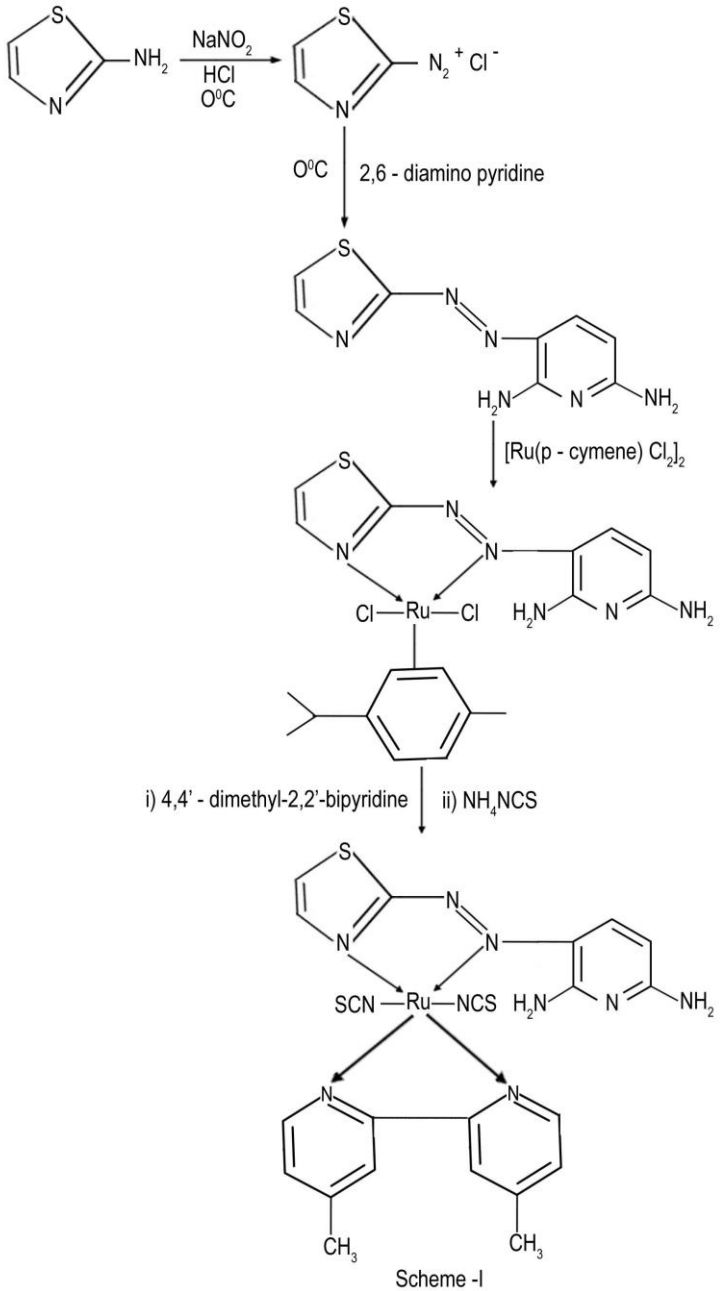
3-(2'-thiazolylazo)-2,6- diamino pyridine(0.127mmol) and dichloro(p-cymene) ruthenium (II) dimer (0.063mmol) in dry DMF were heated at 60^0c for a period of 4h under argon in the dark. Subsequently2,2'- bipyridine-4,4'- dimethyl (0.127mmol) was added and the reaction mixture was heated to 140^0c for another 4h. To the resulting solution was added ammonium thio cyanate (3.821mmol) in water (2ml) and the reaction mixture was further heated for 3h at 150^0c. DMF was removed on rotary evaporator under high vacuum and water (250 ml) was added to get the precipitate. The solid was filtered off, washed with water and diethyl ether and dried under vacuum.

2.3. Synthesis of polyimide :

Ruthenium complex of monomer (1m mol) and 6FDA (1m mol) were dissolved in DMF (20 ml). The solution was stirred at 40^0c under nitrogen for 24h yielding a viscous polyamic acid solution. To this solution acetic anhydride (12 ml) and pyridine (6ml) were added. The stirring was continued at 100^0c for 24h. Then the reaction mixture was poured into methanol, the polymer was filtered and purified by washing with methanol.

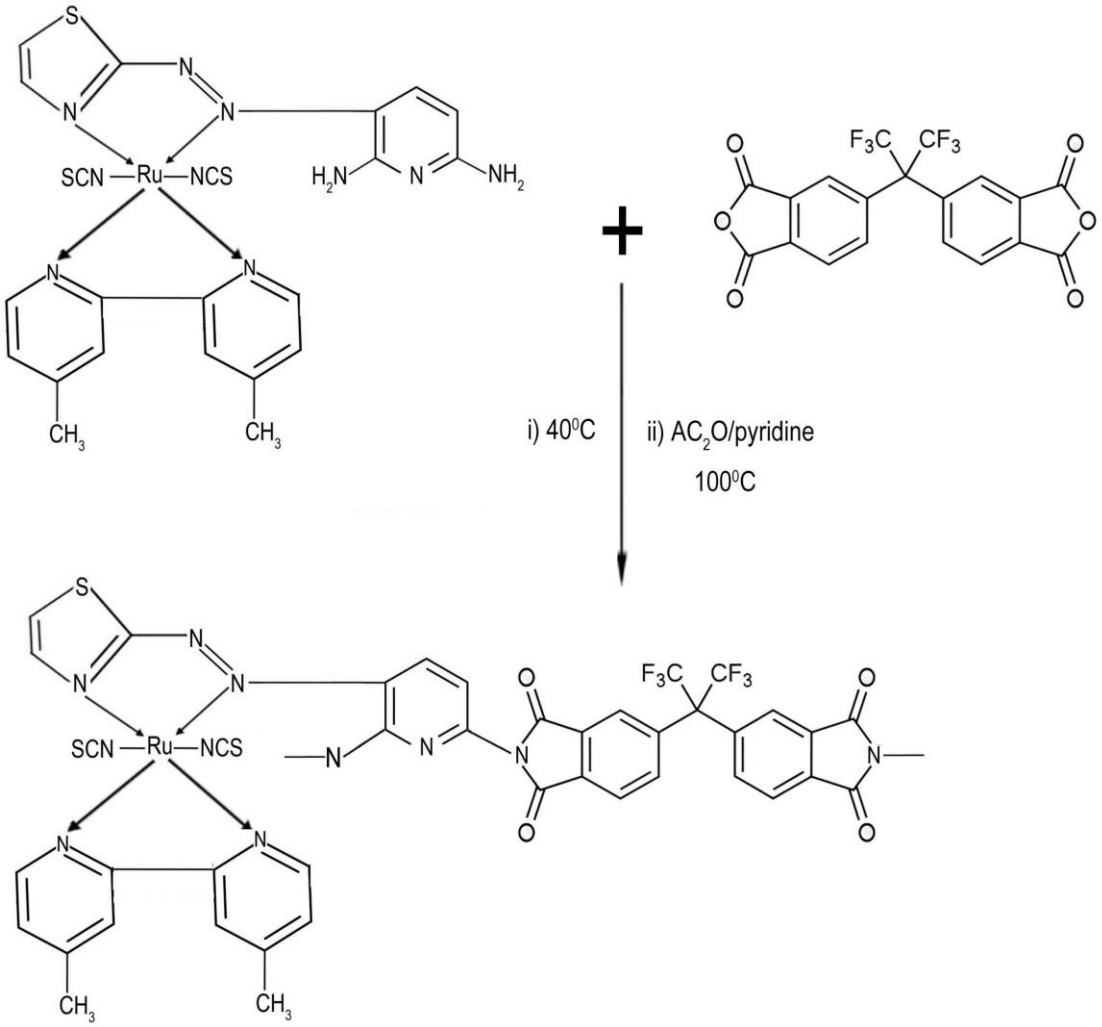
3. Result and discussion :

IR, UV and NMR spectra revealed the successful preparation of monomer and polymer. The monomer was prepared follows : At first azo dye was prepared by treating 2-amino thiazole and sodium nitrite and 6(M) hydrochloric acid then diazonium salt was coupled with well cooled solution of 2,6- diamino pyridine in 4(M) hydrochloric acid. The mixture was stirred in the ice-bath for 1h and then 0.001 (M) sodium hydroxide solution was added into the solution until the P^H=6.0 was reached. A red precipitate began to settle immediately. The solution was filterd and the precipitate was washed with water and air dried. The crude product was purified by recrystallization with a mixture of ethanol/water (3:1) to give red needle shaped crystals. Ruthenium complex was prepared by treating 3-(2'-thiazolylazo)-2,6-diamino pyridine with dichloro (p-cymene) ruthenium (II)dimer in dry DMF were heated at 60^0c for a period of 4h under argon in the dark. Subsequently 4, 4'- dimethyl-2,2'- bipyridine was added and the reaction mixture was heated to 140^0c for another 4h. To the resulting solution was added ammonium thiocyanate in water and the reaction mixture was further heated for 3h at 150^0c. DMF was removed on rotary evaporator under high vacuum and water was added to get the precipitate. The solid was filtered off, washed with water and diethyl ether and dried under vacuum. The synthetic route of monomer was described in scheme - I



Scheme -I

Polyimide was synthesized by treating ruthenium complex with 6FDA in the solvent medium of DMF. The mixture was stirred at 40^0c under nitrogen for 24h yielding a viscous polyamic acid solution. To this solution acetic anhydride and pyridine were added and stirring was continued at 100^0c for 24h. Then the reaction mixture was poured into methanol, the polymer was filtered and purified by washing with methanol. The synthetic route of polymer was described in scheme -II.



Scheme -II

4. Conclusion :

Dye sensitized solar cells have attracted increasing attention as promising alternatives to conventional silicon based solar cells due to their low cost and ease of fabrication. Among a large variety of dyes investigated for DSSC application, ruthenium sensitizer have attracted more attention because of their low lying metal-ligand charge transfer (MLCT) transition that extends into the red and near- infrared region of the solar spectrum. For this reason, we invoked to synthesize a photosensitizing polyimide which can be used in solar cells. The monomer and polymer were characterized by IR, UV and NMR spectra, all of which revealed the successful preparation of polymer.

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