Synthesis Of Photosensitizing Polyester Of Pyridinyl Diimine And Ruthenium (III) Complex .

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Abstract :

Pyridinyl diimine was synthesized by treating 2,6-diformyl pyridine and 4-amino phenol in the solvent medium of ethanol under refluxed for 6h . Ruthenium complex was prepared by treating pyridinyl diimine dissolved in ethanol and ruthenium trichloride trihydrate dissolved in dichloromethane refluxed for 3h. Then the mixture of $Rucl_3$ complex and ammonium thio cyanate in water and DMF mixture was refluxed at 130^0c for 4h. polyester was synthesized by treating ruthenium complex of pyridinyl diimine and terephthaloyl dichloride in presence of triethyl amine in the solvent medium of DMF first at 0^0c then stirred for 6h at room temperature.

Keywords : Pyridinyl diimine , ruthenium complex , polycondensation , polyester.

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 orbitel (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, 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. 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 better cost-efficiency ratio,transperancy, flexibility, ecofriendliness and facile chemical modification. Typically a DSSC consists of four components, namely a mesoporous nanocrystal-like semiconductor, an organic or organometallic dye, an electrolyte and 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 application. Therefore, the metal-free organic dyes are of great interest, considering their facile molecular engineering and stronger light-harvesting capibility than metal complexes. Further, owing to their high molar extinction coefficients 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 ruthenium 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 pyridinyl – 2,6 (4- hydroxy phenyl diimine) :

2,6- diformyl pyridine (0.05 mol) and 4- amino phenol (0.1 mol) were dissolved in ethanol and refluxed for 6h. After cooling the precipitate was filtered and washed with ethanol and water and dried.

2.2 Synthesis of ruthenium complex :

$Rucl_3$ (130 mg ,0 .84 mmol) was dissolved in ethanol (30 ml) and the solution was stirred for 2 min. at 50^0c. To this solution , a solution of ligand (0.51 mmol) in dichloro methane (20 ml) was added, and the mixture was refluxed for 3h. The solution was concentrated to 10 ml and then cooled to room temperature. The precipitate was filtered , washed with cold ethanol and the product was air dried .

A mixture of $Rucl_3$ complex (0.39 mmol) , aqueous ammonium thio cyanate (113 mmol) in water (5ml) in DMF (25 ml) was refluxed at 130^0c for 4h under argon atmosphere. The reaction mixture was allowed to cool and the solvent volume was reduced on a rotary evaporator to about 5 ml . Water was added to the flask, and the insoluble solid was filtered and air dried .

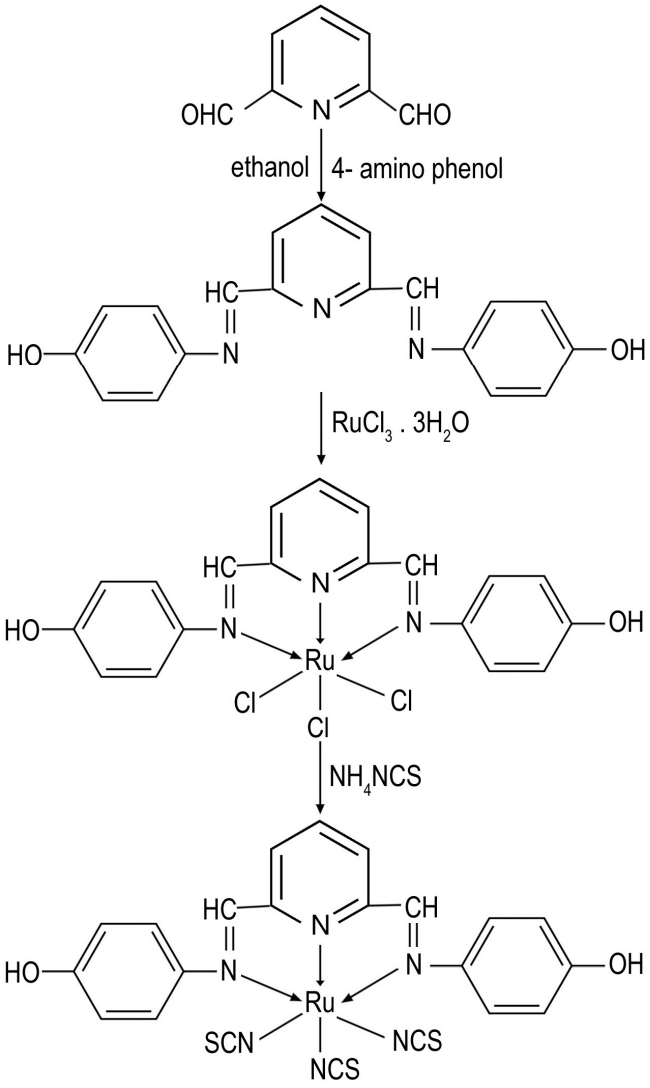
2.3 Synthesis of polyester:

A typical synthesis procedure for the preparation of polyester was conducted in three-necked round- bottom flask equipped with a nitrogen inlet , a condenser, and a magnetic stirrer bar. The flask was charged with ruthenium complex (2 mmol) In 20 ml of DMF and 0.8 ml of triethyl amine. A solution of terephthaloyl dichloride (2 mmol) in 10 ml DMF was added drop wise at 0^0c. The reaction was stirred for 6h at room temperature. The solution was then poured into water, and the precipitate was filtered and washed several times with the solution of sodium bicarbonate. The solid product was then dried in a vacuum oven at 60^0c.

3. Results and discussion:

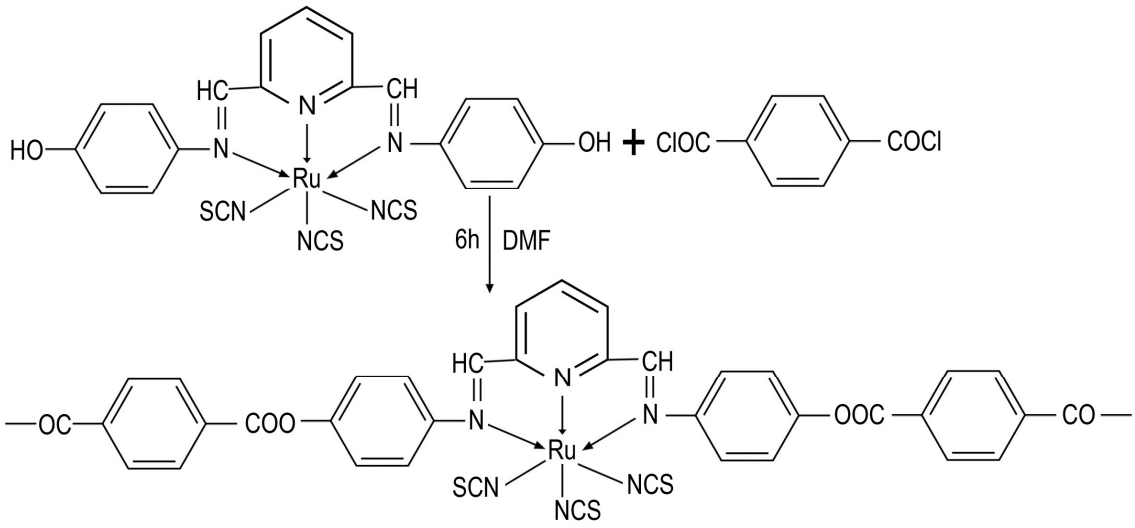
IR, UV and NMR spectra revealed the successful preparation of the polymer. The monomer was synthesized as follows At first, pyridinyl-2,6-(4-hydroxy phenyl diimine) was synthesized by the treatment of 2 ,6-diformyl pyridine and 4-amino phenol dissolved in ethanol and refluxed for 6h. After cooling , the precipitate was filtered and washed with ethanol and water and dried. Ruthenium complex of monomer was synthesized by dissolving $Rucl_3$ in ethanol stirring for 2 min at 50^0c and the monomeric ligand in dichloromethane was added and the solution was refluxed for 3h. Then the solution was concentreated to 10 ml and cooled to room temperature . The precipitate was filtered, washed with cold ethanol and the

product was air dried . Then, a mixture of $Rucl_3$ complex , aqueous ammonium thiocyanate in water (5ml) and DMF (25 ml) was refluxed at 130^0c for 4h under argon atmosphere . The reaction mixture was allowed to cool and the solvent volume was reduced on a rotary evaporator to about 5 ml. water was added to the flask, and the insoluble solid was filtered and air dried. The synthetic procedure of monomeric ligand and its ruthenium complex was represented in scheme -I.



scheme -I

A typical synthesis procedure for the preparation of polyester was conducted in three-necked flask equipped with a nitrogen inlet, a condenser, and a magnetic stirrer bar. The flask was charged with ruthenium complex and triethyl amine in 20 ml of DMF. A solution of terephthaloyl dichloride in 10 ml DMF was added dropwise at 0^0c. The reaction was stirred for 6h at room temperature. The solution was then poured into water, and the precipitate was filtered and washed several times with the solution of sodium bicarbonate . The solid product was then dried in a vacuum oven at 60^0c. The synthetic route of polyester was represented 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 polyester which can be used in solar cells. The monomer and the polymer were characterized by IR, UV and NMR spectra, all of which revealed the successful preparation of the polymer .

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