

Synthesis Of Photosensitizing Polymer of Complex Between 4-(2'-thiazolylazo)-2- methoxy aniline And Ruthenium(II)

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Abstract:

2-amino thiazole was diazotized with sodium nitrite and 6(M) hydrochloric acid at 0°C. Then it was coupled with 2-methoxy aniline. The mixture was stirred for 1h then 0.001(M) sodium hydroxide solution was added into the mixture until $P^H=6.0$ was reached. Ruthenium (II) complex was prepared by adding the above dye to the hot solution of $[Ru(bpy)_2Cl_2]$ in ethanol and refluxed for 2h. After removal of excess solvent under reduced pressure, ammonium hexafluoro phosphate was added to the solution. The product was collected by filtration and then washed with ethanol and ether repeatedly. The product was purified by column chromatography using silica gel column. Vinyl monomer of the complex was prepared by treating ruthenium complex with methacryloyl chloride in presence of triethyl amine in the solvent medium of THF at 0°C for 3h and then at room temperature for 50h. Polymerization was carried out by treating the vinyl monomer with styrene in the solvent medium of DMF at 110°C for 80h.

Keywords:

4-(2'-thiazolylazo)-2- methoxy aniline, ruthenium complex, vinyl monomer, polymerization.

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I. Introduction:

The chemistry of ruthenium (II) complexes containing the azoimine functional unit has been receiving considerable attention, because of the variety of advantages exhibited by its complexes. This functional group azoimine, is pi-acidic in character. The advantage of azoimine functional unit is that it has strong ability to stabilize low valent metal redox states, such as Ru(II), Os(II), Pd(II), Pt(II). Thus the azoimine functionalized ligand complexes enamoured us to study its chemistry and to designing a molecular architecture with this function. In addition, the ruthenium (II) complexes with azoimine ligands were investigated because of their potential application in many chemical reactions. The thiazolylazo compound acts as a bidentate ligand that can coordinate to a metal ion through the lone electron pairs of the thiazol and the azo nitrogen atoms.

Arylazo heterocycles containing azoimine group of N, N-chelating system and their coordination chemistry are of current interest. The azoimine function has speciality to stabilize lower oxidation state of metal ions and tune the redox and spectral properties of the metal centre. Thiazolylazo compounds particularly, are important because they can form different types of coordination compounds with transition metals due to the several electron rich donor centers with unusual structural and chemical properties. The literature survey suggests that the structural chemistry of transition metal complexes of azo dyes containing nitrogen donor atoms exhibit large variations. The variation in the structural aspects can be related with nature of donor atom, the structure of ligand and also the metal ligand interaction (MLCT)

The past few years have seen a rapid development in the chemistry, biochemistry and photophysics of azoimine complexes of ruthenium. Azoimine complexes of ruthenium are extensively used as photosensitizers and for biological sensing. They are also used in dye sensitized solar cells. They are also promising candidates for incorporating into low voltage, single-layer, solid state electroluminescent devices, such as light emitting diodes (LEDs), as they have high photo – redox efficiencies.

Electroluminescent devices using transition metal dyes typically used unsubstituted and peripheral hydrogen substituted poly pyridyl complexes of ruthenium and other transition metal complexes. However, nitrogen rich heterocyclic ligands, complexing with platinum, iridium and other transition metals have been extensively used to synthesize light-emitting self-assembled materials. In order to explore the activity of nitrogen rich heterocyclic ligands in electroluminescent devices, we developed this. The synthesized polymer display metal to ligand charge transfer (MLCT) excitation band in the visible region

II. Experimental:

2.1 Synthesis of 4 – (2'- thiazolylazo) -2- methoxy aniline:

1.0g of 2- amino thiazole was dissolved in 16ml 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 2- amino thiazole solution while stirring with a glass rod under low temperature (0^oc). The solution of diazonium salt was slowly added while stirring into a well cooled solution of 2 - methoxy aniline (1.0g) in 20ml 4(M) hydrochloric acid. The mixture was stirred in the ice- both for 1h and then 0.001(M) sodium hydroxide solution was added into the mixture until P^H=6 was reached. A 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.

2.2. Synthesis of ruthenium complex:

4-(2'- thiazolylazo)-2- methoxy aniline(48.44mg, 0.207mmol) was added to a hot solution of dichloro bis (bipyridine) ruthenium (II) (100mg, 0.207mmol) in ethanol. On subsequent heating under reflux for 2h, the volume of the solution was reduced under reduced pressure, and ammonium hexafluoro phosphate was added to solution. The product was collected by filtration. The product was purified by column chromatography using silica gel column.

2.3. Synthesis of vinyl monomer:

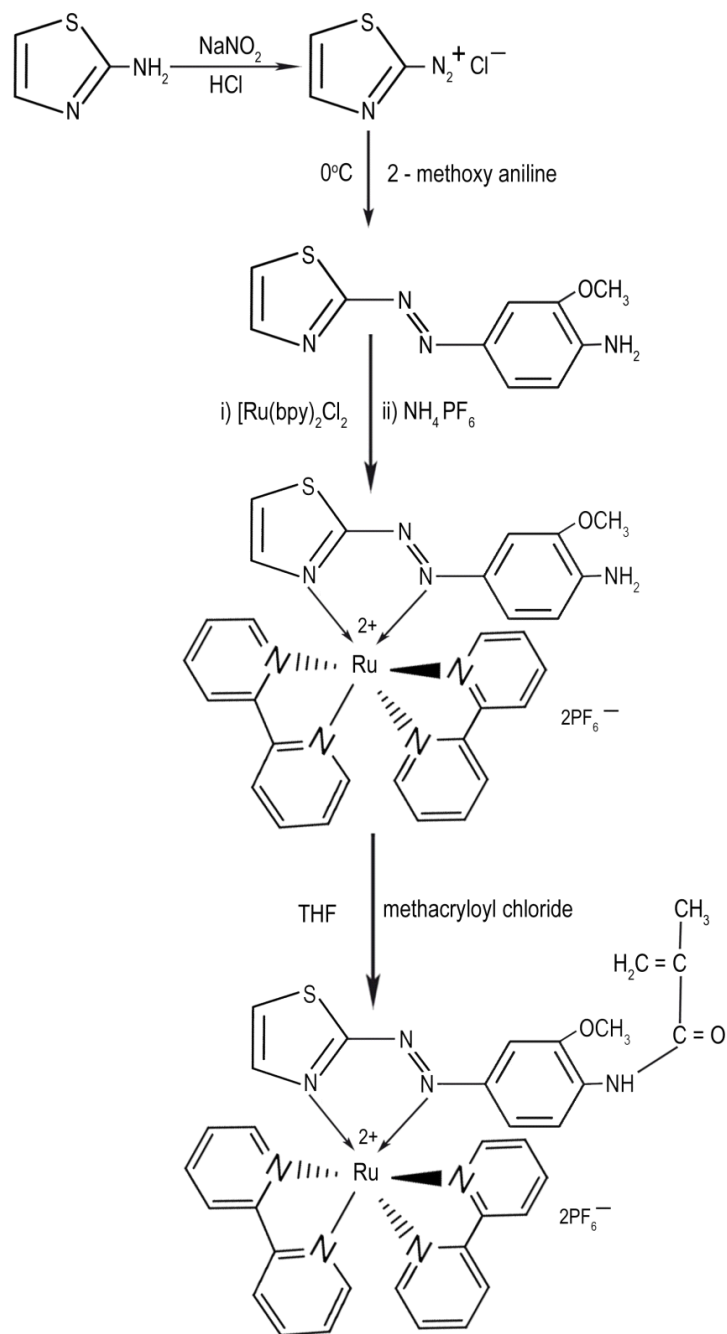
Ruthenium complex (0.52g, 0.83mmol) was dissolved in 20ml of THF by stirring it at room temperature under nitrogen. Triethylamine(0.84g, 8.36mmol)was added to the solution and stirred. Methacryloyl chloride (0.13g,1.24mmol)was added in drop wise to the solution. The resulting solution was stirred at room temperature under nitrogen atmosphere for 50h. The solution was poured in water and extract with dichloromethane. The organic layer was washed with water and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure. The solid was purified by column chromatography.

2.4. Synthesis of polymer:

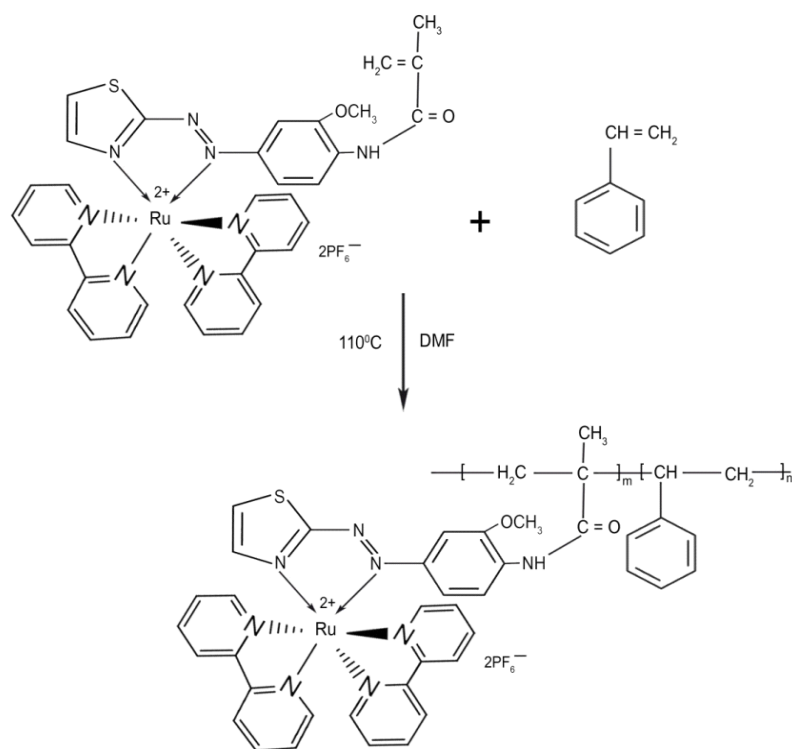
Vinyl monomer (2.61g,3.77 mmol), styrene (0.39g,3.75mmol) and AIBN (2g,12.19mmol) were dissolved in dry DMF (40ml). The reaction was carried out at 110^oc for 80h under nitrogen. The polymer was precipitated out in methanol, filtered, dried under vacuum.

III. Result and discussion:

4-(2'- thiazolylazo)-2- methoxy aniline was synthesized as follows: 2- amino thiazole was diazotized with sodium nitrite and 6(M) hydrochloric acid at 0^oc. Then it was coupled with 2- methoxy aniline. The mixture was stirred for 1h then 0.001(M) sodium hydroxide solution was added into the mixture until P^H=6 was reached. A 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. Ruthenium (II) complex was prepared by adding the above dye to the hot solution of dichloro bis (bipyridine) ruthenium (II) in ethanol and refluxed for 2h. The volume of the solution was reduced under reduced pressure, and ammonium hexa fluoro phosphate was added to solution. The product was collected by filtration. The product was repeatedly washed with ethanol and ether. The product was purified by column chromatography using silica gel column. Vinyl monomer of the complex was prepared by treating ruthenium complex with methacryloyl chloride in presence of triethyl amine in the solvent medium of THF at room temperature for 50h. The solution was poured in water and extract with dichloromethane. The organic layer was washed with water and dried over anhydrous magnesium sulphate. The solvent was removed under reduced pressure. The solid was purified by column chromatography. The synthetic route of monomer was represented in scheme-I.



Scheme – I



scheme – II

Polymerization was carried out by treating the vinyl monomer with styrene in the solvent medium of DMF at 110°C for 80h under nitrogen. Polymer was precipitated out in methanol, filtered, dried under vacuum. The synthetic route of polymer was represented in scheme – II

IV. Conclusion:

We have synthesized new photosensitizing polymer of complex between 4-(2'-thiazolylazo)-2-methoxy aniline and ruthenium(II). The monomer and polymer were characterized by IR, UV and NMR spectra. This polymer can be used in dye sensitized solar cell. 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. This polymer can also be used in electroluminescent devices.

References:

- [1] Kippelen B, Tamura K, Peyghambarian N, Padias AB, Hall Jr. HK. Phys. Rev B 1993, 48 (15): 10710.
- [2] Yu L, Chan WK, Peng Z, Gharavi A. Acc. Chem. Res. 1996, 29:13.
- [3] Zhang Y, Wada T, Wang L, Aoyama T, Sasabe H. Chem. Commun. 1996, 2325
- [4] Barrett C, Chowdhury B, Natansohn A, Rochon P. Macromolecules 1998, 31, 4845
- [5] Wright D, Diaz-Garcia MA, Caspersen JD, DeClue M, Moerner WE, Twieg RJ. Appl. Phys. Lett. 1998, 73(11), 1490.
- [6] Cox AM, Blackburn RD, West DP, King TA, Wada FA, Leigh DA. Appl. Phys. Lett. 1996, 68(20), 2801.
- [7] Zhang Y, Ghosal S, Casstevens MK, Burzynski R. J. Appl. Phys. 1996, 79 (12), 8920.
- [8] Silence SM, Scott JC, Stankus JJ, Moerner WE, Moylan CR, Bjorklund GC, Twieg RJ. J. Phys. Chem. 1995, 99, 4096.
- [9] Moon H, Hwang J, Kim N, Park SY. Macromolecules 2000, 33(14), S116.
- [10] Moon H, Kim N, Park SY. Nonlinear Optics 1999, 20, 347.
- [11] Meerholz K, Volodin BL, Sandalphon, Kippelen B, Peyghambarian N. Nature 1994, 371(6), 497.
- [12] Bolink HJ, Krasnikov VV, Malliaras GG, Hadziioannou G. J. Phys. Chem. 1996, 100, 16 356.
- [13] Zhang Y, Spencer CA, Ghosal S, Casstevens MK, Burzynski R. Appl. Phys. Lett. 1994, 64, 1908.
- [14] Han SH, Wu JW. J. Opt. Soc. Am B 1997, 14, 1131.
- [15] Sutter K, Gunter P. J. Opt. Soc. Am B 1990, 7, 2274
- [16] Walsh CA, Moerner WE. J. Opt. Soc. Am B 1992, 9, 1642
- [17] Centore R, Panunzi B, Roviello A, Sirigu A, Villano P. J. Polym. Sci. Part A Polym. Chem. 1996, 34, 3203.