



Review Paper

Synthesis and Photophysical Application of Functionalised 2,2':6',2''-Terpyridine Metal Complexes

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Abstract

This report outlines the progress to date in preparing derivatives of 2,2':6',2''-Terpyridine and its metal complexes that shows spectroscopic and luminescence properties. Derivatives investigated are of the type 4'-Functionalized- 2,2':6',2''-Terpyridines, 4'-(4''-bromomethyl phenyl)-2,2':6',2''-terpyridine, 4'-aryl-2,2':6',2''-terpyridines, 1,3-bis(2,2':6',2''-terpyridin-4'-yl)benzene dichloromethane solvate. and 5,5''-bis (hydroxytetramethylenoxy methyl)-2,2':6',2''-terpyridine. The reported papers having complexes of these ligands with different metal ions like Co(II), Co(III), Cr(III), Ni(II), Cu(II), Pt(II), Ru(II), Ir(II), Pd(II), Fe(II), Zn(II) have been reviewed. The photophysical applications of these ligands and their metal complexes are of the type construction of photochemical molecular devices, photosensitized component, Colorimetric and Luminescence pH Sensors, supramolecular recognition centers, biosensor etc. which has been reported by different authors are also reviewed.

Keywords: 2,2':6',2''-Terpyridine, Functionalized- 2,2':6',2''-Terpyridines, Metal complexes, photophysical applications.

Introduction

The coordination chemistry plays a vital role in supramolecular chemistry and photophysical applications. Elements like oxygen, nitrogen and phosphorus atoms are used in reaction with transition metals. An extraordinary importance of nitrogen ligand is the chemistry of oligopyridines which have attracted special interest in coordination chemistry. Burstall and Morgan reported the first synthesis of 2, 2':6', 2''-terpyridine¹. Krohnke synthesized pyridines² and other substituted pyridines like terpyridines³ which were used as distinguished building blocks in supramolecular chemistry because of their p-stacking ability, and directed H-bond formation. 2, 2':6', 2''-Terpyridine has been reacted with many metals to prepare complexes. Substituted- 2,2':6',2''-terpyridines (tpys) ligands have drawn attention due to their ability to form complexes with transition metals, and are applied extensively in coordination chemistry⁴. The applications of tpys have been found in various fields such as supramolecular chemistry⁵ asymmetric catalysis⁶ photosensitization⁷ and antitumor chemo-therapeutics⁸. In 1932 Morgan and Burstall heated pyridine and anhydrous iron(III) chloride in an autoclave⁹ and Terpyridine was one of 20 products of this reaction. The synthesis has been developed to give more specific results and better yields. The use of aryl substituents in the 4'- position gives a molecule which can be used in the colorimetric determination of iron(II) as well as having the potential for use in clinical chemistry. There are examples of the use of terpyridine ligands in the preparation of luminescent materials and these have potential as luminescent protein labels¹⁰. In this review, an overview of synthesis of

functionalized 2,2':6', 2''-terpyridine and its metal complexes are given. We have also reviewed their photophysical applications.

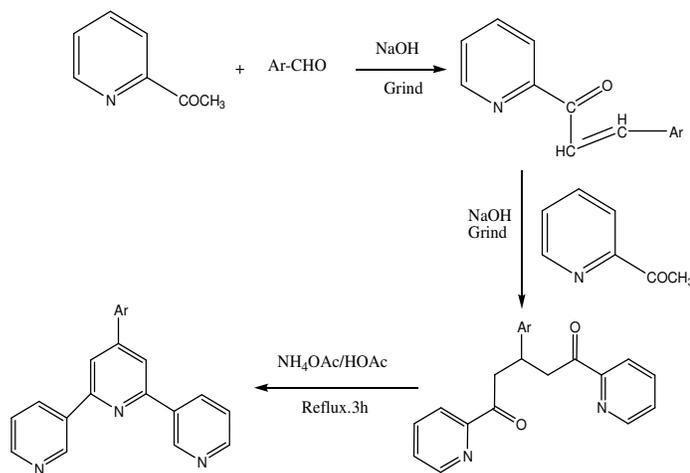
Material and Methods.

The synthesis of 2, 2':6', 2''-terpyridines involve two general procedure, either we can synthesize the central ring or we may do the coupling of three pyridine rings. A number of methods have been developed for the synthesis of this ligand which can be categorised as i condensation method ii pyrolysis; iii Tohd method iv metal mediated coupling reaction; v cycloaddition or Sauer method.

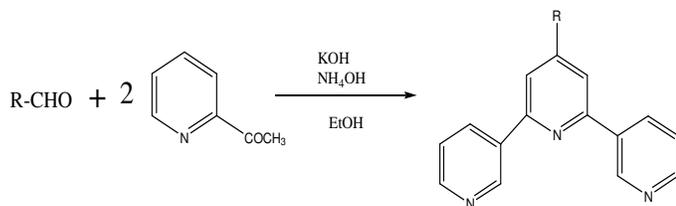
Synthesis of 4'-Functionalized 2, 2':6', 2''-Terpyridine: New 4'-Functionalized 2, 2':6', 2''-Terpyridines were synthesized in large scale functionalized in the 4'-position, by the well-known nucleophilic substitution reaction of alkoxides. The alkyl-chain functionalized terpyridines synthesized form ordered two-dimensional structures on HOPG (Highly Ordered Pyrolytic Graphite), which were investigated by STM and have applications in macromolecular chemistry and nanoscience¹¹.

Synthesis of β -cyclodextrin-based terpyridine derivatives: A terpyridine analogue has been prepared by the coupling of 4'-(4''-bromomethyl phenyl) - 2, 2':6', 2''-terpyridine with mono-6-hydroxy permethylated β -cyclodextrin. The cyclodextrin dimmer joining a 4'-phenyl-2, 2':6', 2''- terpyridine spacer on the primary faces was synthesized by reaction of 4'-phenyl-2, 2':6', 2''-terpyridine-6,6'-dicarbonitrile with an excess of 6-deoxy-6-O-tosyl- β -cyclodextrin¹².

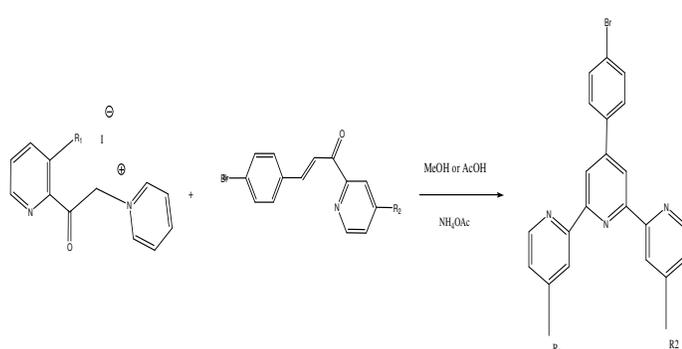
2.3 Synthesis of 4'-aryl-2,2':6',2''-terpyridine: A high yield aqueous Krohnke reaction process has been used for the synthesis of 4'-aryl-2,2':6',2''-terpyridines via a one-pot procedure by taking the starting material 2-acetylpyridine with aromatic aldehyde in presence of ammonium acetate under microwave irradiation or conventional heating conditions. This method is convenient, economic and environmental friendly. The methods to synthesize terpyridines were as per Schemes 1-3¹³.



Scheme-1



Scheme-2



Scheme-3

Synthesis of 4'-(4-Bromophenyl)-2,2':6',2''-terpyridine: 4'-(4-Bromophenyl)-2,2':6',2''-terpyridine was prepared on a large scale from 2-[3-(4-bromophenyl)-1-oxoprop-2-enyl]pyridine and N-[2-oxo-2-(2-pyridyl)-ethyl] pyridinium iodide. This

synthesis provides several related novel indolizinium derivatives, including 1-[3-(4-methylphenyl) indolizin-1-yl-imino]-3-[4-methylphenyl]-1Hindolizinium hexafluoro phosphate, whose crystal structure has been determined¹⁴.

Synthesis of 5,5''-bis(hydroxytetramethylenoxymethyl)-2,2':6',2''-terpyridine: 5,5''-bis(hydroxytetramethylenoxymethyl)-2,2':6',2''-terpyridine was synthesized in high yield utilizing organotin intermediates and Stille coupling procedures. Different functionalized pyridine precursors were prepared¹⁵.

Synthesis of 1,3-bis(2,2':6',2''-terpyridin-4'-yl) benzene dichloromethane solvate: 1,3-bis(2,2':6',2''-terpyridin-4'-yl) benzene dichloromethane solvate, C₃₆H₂₄N₆.CH₂Cl₂, is a new ligand suitable for bridging two metal centres. Its two terpyridine units are linked in a unique arrangement. The two terpyridine units are related by crystallographically imposed twofold symmetry, forming a 30.02 (8)⁰ dihedral angle with the phenylene core, having quite coplanar pyridine rings within. The solvent molecule is disordered over the twofold axis¹⁶.

Synthesis of 4'-(4-bromophenyl)-2, 2':6', 2''-terpyridine from 2-acetylpyridine: 4'-(4-bromophenyl)-2, 2':6', 2''-terpyridine has been synthesized from 2-acetylpyridine and 4-bromobenzaldehyde using a two step aldol condensation in which the yield percentage was too high. Here the intermediate azachalcone was isolated and reacted with N-[2-oxo-2-(2-pyridyl) ethyl] pyridinium iodide, (prepared from 2-acetylpyridine) using ammonium acetate both as a base and as a ring closure agent¹⁷.

Synthesis of metal complexes of functionalised 2, 2':6',2''-Terpyridine. Synthesis of Ru (terpy)-based binuclear complexes: Two new Ru (terpy)-based binuclear complexes were synthesized in which the butadiynylene bridge is interspersed with either a 1,4-phenylene or a 5,5'-(2,2'-bipyridylene) spacer. Relative to [Ru(terpy)₂]²⁺. Both are strongly emissive and have high luminescence quantum yield¹⁸.

Synthesis of [Ru(terpy)(terpy-rotaxane)]²⁺ complexes: The rotaxane ligands were used in the preparation of a series of heteroleptic [Ru(terpy)(terpy-rotaxane)]²⁺ complexes. These complexes exhibit a luminescence band in the near infrared region in contrast with the parent [Ru(terpy)₂]²⁺ complex, at room temperature and a relatively long lived triplet metal-to-ligand charge-transfer (MLCT) excited state, due to the presence of strong-electron-acceptor pyridinium substituents on one of the two terpy ligands. These metal complexes are used for the construction of photochemical molecular devices with a wire-type structure¹⁹.

Synthesis of Cu(II) terpyridine complexes: The Cu(II) complexes were prepared with tridentate ligands such as iminodiacetate, 2,6-dipicolinate, diethylenetriamine, terpyridine, for identification of basic neutral species like imidazole derivatives in water to bind ureas and amides in methanol, which is an organic solvent most resemblance to water²⁰.

Synthesis of [Cu(H₂O)₂(TERPY)]-[Cu(TERPY)(ADP)] [H₂ADP]16H₂O: Highly hydrated single crystals containing adenosine 5'-diphosphate and copper(II) ions with the stoichiometry [Cu(H₂O)₂(TERPY)]-[Cu(TERPY)(ADP)] [H₂ADP]16H₂O, has been prepared and characterized. The existence of supramolecular networks *via* hydrogen bonding and stacking interactions for adenosine 5'-diphosphate has been established²¹.

Synthesis of Mononuclear Cu(II) terpyridine complexes: Mononuclear copper(II) terpyridine complexes, [Cu(tpy)-Cl]Cl (**1**) and [Cu(itpy)Cl]Cl (**2**) (tpy = tolylterpyridine and itpy = imidazolylterpyridine) were synthesized and characterized. From the gel electrophoresis experiments, it is inferred that both complex **1** and **2** cleave plasmid DNA in the presence of ascorbic acid and the cleavage efficiency of complex **1** is greater than that of complex **2**²².

Synthesis of mixed ligand-Zinc (d¹⁰) complex: A mixed ligand-zinc (d¹⁰) complex containing coordinated peroxy ion and 2,2',2''-terpyridine shows fluorescence in the visible region (473 nm) on excitation at 390 nm in aqueous medium at room temperature. The unusual phenomenon of enhancement of this fluorescence intensity on addition of some transition metal ions has been verified which are commonly used as fluorescent quenchers²³.

Synthesis of Ru (II) and Os(II) complexes of triarylpyridinio-derivative: A new class of triarylpyridinio-derivative was designed as a novel category of electron-acceptor -substituted proto-photosensitizing molecule. Their Ru(II) and Os(II) complexes act as photosensitized component²⁴.

Synthesis of [Ir(terpy) (L) Cl]²⁺: Mixed ligand complexes in the form of [Ir(terpy)(L)Cl]²⁺ were prepared and their electrochemical and phosphorescent properties were investigated. The ligands were terpyridine and bipyridine derivatives²⁵. **Synthesis of Fe(II) supramolecular polymers containing hydroxy-functionalized terpyridine as initiator.**

Using a hydroxy-functionalized terpyridine as initiator, a poly (ε-caprolactone) containing one terpyridine endgroup was prepared by tin octanoate-catalyzed controlled ring-opening polymerization. The ÷-hydroxy group of this polymer was subsequently reacted with an isocyanato-ureidopyrimidinone, resulting for the first time in polymers bearing a metal-coordinating ligand on the one and a hydrogen-bonding unit on the other chain end. Hydrogen-bonded supramolecular dimers were shown to be present in chloroform solution. The subsequent addition of iron(II) ions resulted in the formation of high molecular weight supramolecular polymers with novel properties resulting from the combination of both types of noncovalent interactions in the main chain, as could be shown using capillary viscosimetry and rheometry²⁶.

Synthesis of Monoligand-nickel(II) and the bisligand-

nickel(II) complexes of 2,2',2-terpyridine: Monoligand-nickel(II) and the bisligand-nickel(II) complexes of 2,2',2-terpyridine with nickel(II) ion were prepared and the rate at which they react to form the complex has been determined in DMSO solution. Ni(terpy)Cl, was isolated, and used to study the rate of formation of biscomplex. The second-order rate constants were found to parallel the rates of DMSO exchange, determined using N.M.R. techniques, from the respective paramagnetic nickel species²⁷.

Synthesis of [(2,2':6', 2''- terpyridine) Pd (C₃H₅)] X: The palladium allyl complexes [(2,2':6', 2''- terpyridine) Pd(C₃H₅)]X (X⁻ = BF₄⁻, X⁻ = ClO₄⁻) were synthesized and characterized. The molecular structures of the complexes were determined by X-ray crystallography, whereas a variable-temperature ¹H NMR analysis shows that the complex is fluxional²⁸.

Synthesis of Co(II) and Co(III) complexes of imidazole terpyridine (Itpy): Co(II) and Co(III) complexes of tridentate ligand, imidazole terpyridine (Itpy), have been synthesized and characterized by both spectroscopic and electrochemical techniques. Both the complexes belong to monoclinic crystal system, with the two Itpy ligands coordinated to the central metal ion which is observed from Single crystal Xray diffraction studies. The binding behavior of both the cobalt complexes to calf thymus DNA has been investigated by UV-Vis, fluorescence spectroscopy, viscosity and electrochemical measurements. The results suggest that both the complexes bind to DNA through intercalation²⁹.

Synthesis of Back-to-back dinuclear platinum terpyridine complexes: Back-to-back dinuclear platinum terpyridine complexes with different substituents on the bridging ligand were synthesized and characterized. Their electronic absorption, emission and triplet transient difference absorption were systematically investigated. All complexes show strong MLCT/ILCT absorption bands in the visible region, which appreciably red-shifts when electron-donating substituents were attached on the conjugated bridge and blue-shifts when electron-withdrawing substituents were present³⁰.

Synthesis of rod-like dinuclear Ru(II) polypyridine compounds: Three new rod-like dinuclear Ru(II) polypyridine compounds have been prepared and characterized. Their absorption spectra, redox behaviour and photophysical properties have been investigated³¹.

Photophysical application of Functionalised 2,2':6',2''-Terpyridine metal complexes. Photophysical properties of terpyridine complexes possessing Pt(II): Structure-property relationships in square-planar terpyridine complexes possessing Pt(II) metals depend upon substituents that are introduced to the terpyridine ligand. As a result photophysical properties can be accessed, thereby finding new applications in molecular sensing as well as construction of supramolecular architectures. A

number of extraordinary photoluminescent Pt(II) terpyridine complexes consisting of alkynyl groups, as co-ligands, has been reported³². Pt(II) complexes with aryl-modified and fused terpyridine ligands have been reported which shows their luminescent properties at ambient temperature³³. A series of platinum(II) terpyridyl alkynyl complexes derivatized with basic amino functionalities, have been synthesized and characterized. Their photophysical responses at various acid concentrations were studied. These complexes function as colorimetric and luminescence pH sensors which was observed from the colour changes and luminescence enhancement upon introduction of acid³⁴.

Photophysical properties of terpyridine-based cruciform-Zn(II) complexes: The target compound containing two terpyridine units has been synthesized which on interaction with metal cation gives emission color changes. In the case of zinc triflate the compound forms complexes, which could be used to detect halide ions. This terpyridine-based cruciform-Zn(II) complexes act as anion-responsive fluorophores³⁵.

Photophysical properties of terpyridine complexes possessing Ru(II): A new bridging ligand, 1'', 4''-bis(2,4-dipyrid-2'-yl-1,3,5-triazin-6-yl)benzene (bis-dpt), has been synthesized, which contains two electron-deficient dpt motifs. The importance of this bridging ligand is that it can allow better electron delocalisation over the two dpt units due to the co-planar arrangement of the two triazines bonded by the central phenyl ring. A new dinuclear rod like Ru(II) complex has been prepared which shows improved photophysical and electrochemical properties, such as the ability to store several electrons on the bridging ligand³⁶.

Photophysical properties of dinuclear Ir(II) complex: The photophysical properties of a cyclometalated dinuclear iridium complex, (ppy)₂Ir(mu-BPB)Ir(ppy)₂ [ppy = 2-phenylpyridine, BPB = 1,4-bis(pyridin-2-yl)benzene], have been investigated³⁷.

Conclusion

The investigation of the preparation of functionalized terpyridine involve a number of functional groups like methyl, carbonyl, carboxylate, halogenide, amines, oxime, hydroxylamine, azide, azo, nitro and oxypyridines especially at C(4'). These substituted terpyridines on further reaction produce many other derivatives which has been utilised to form complex with the metal ions like Co(II),Co(III),Cr(III),Ni(II),Cu(II), Pt(II),Ru(II),Ir(II),Pd(II),Fe(II),Zn(II). These functionalized terpyridine and their metal complexes have several photophysical applications and have been used as photochemical molecular devices, photosensitized component, Colorimetric and Luminescence pH Sensors, supramolecular recognition centers, biosensor etc. The photophysical property of these ligands and their metal complexes have been reviewed.

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