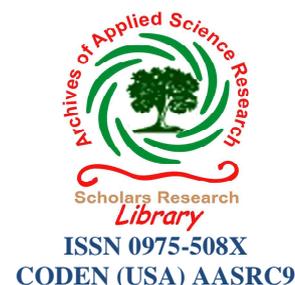




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Ruthenium dyes with donor and acceptor moieties for TiO₂ solar cells

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ABSTRACT

Dye sensitized solar cell with bipyridyl ligands such as N₃ dye has absorption upto 800nm and the co-efficient of absorption is less. So this paper explains about the synthesis and characterization of new terpyridine complexes with substitution at 4th position to replace black dye and subsequently ligated to Ruthenium metal covering the longer absorption region of solar spectrum from higher to lower energy with good absorption co-efficient. Synthesis of new Ru(II) complexes containing donor and acceptor moieties along with anchoring group to bind the surface of TiO₂ was the main objective of this paper.

Keywords: Terpyridine complexes Synthesis, Characterization, Solar cells

INTRODUCTION

Dye sensitized solar cells came into lime light with a great deal of interest among chemists after the discovery by Professor Gratzel's group. The dye sensitized solar cells provides a technically and economically credible alternative concept to the photovoltaic devices in recent days. Since the discovery of ruthenium dye sensitized TiO₂ solar cell, several attempts have been made to increase the efficiency. One among the major factors is the improvement of photocurrent. The photochemistry of Ru(II)-polypyridyl complexes has been at the centre stage for many years[1-7]. Owing to their unique combination of attractive properties such as high thermal and photochemical stability, strong absorption in visible region, moderate long lived triplet state generated through intersystem crossing and ability to undergo both reductive and oxidation electron transfer processes. Ruthenium complexes containing bipyridyl ligands such as N₃ dye has absorption upto 800nm. So, in order to increase the absorption edge and co-efficient of absorption to 1000nm, terpyridyl complexes of ruthenium have been employed, viz., "black dye".

MATERIALS AND METHODS

All raw materials were purchased from Aldrich, E Merk and SD fine Chemicals Co. and were used as received without any further purification. Solvents were dried by standard literature methods before being distilled and stored under nitrogen over 4 Å molecular sieves.

The Ru(II) complex was readily prepared in three steps by first reacting RuCl₃.H₂O with 1 equivzlent of R-terpyridine (F1,F2,F3) which itself was synthesized by a cross-coupling reaction. The resultant complex Ru(F)Cl₃ was converted to [Ru(F)(L1,L2,L3)] which afforded the desired complex. An analytically pure sample of Ru complex was prepared by multiple recrystallisations from acetonitrile/diethylether or ethanol/methanol, DMF,

Chloroform etc. The compound, after isolation as was relatively soluble in most polar organic solvents at room temperature. It was stable toward prolonged storage in ambient light.

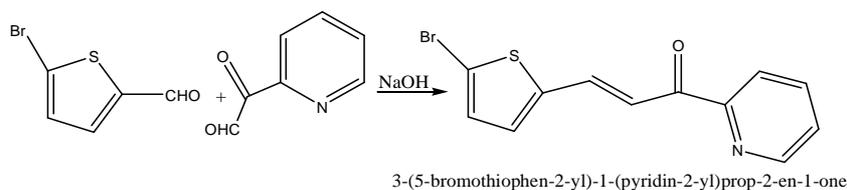
2.1. Ligand Synthesis(F1,F2,F3)

The terpyridine ligand was synthesized in a stepwise procedure.

Step 1

Preparation of 2-(5-Bromothiophen-2-yl)-1-pyridin-2-yl-propenone (A)

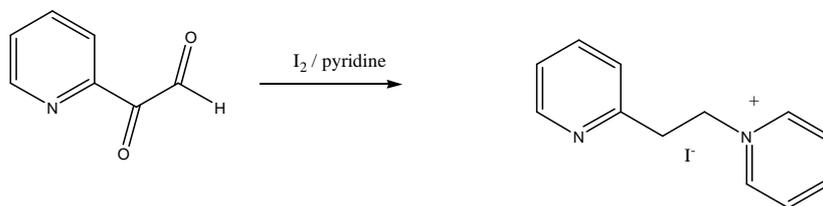
To an ice-cooled methanolic solution of 5-Bromo-2-thiophenecarboxaldehyde (2.01 g, 10 mmol) and 2-acetyl pyridine (1.21 g, 10 mmol) was added dropwise aqueous NaOH (0.4 g, 10 mmol) solution. After slow addition of the base for about 20 min, the mixture was allowed to attain room temperature and stirred for 2 h. The pale yellow precipitate was filtered off and recrystallized from ethanol. Yield: 3.0 g (85%).



Step 2

Preparation of 1-(2-Oxo-2-pyridin-2-yl-ethyl) pyridinium iodide (B)

Added drop wise the iodine (12.65 g, 50 mmol) solution in dry pyridine (60 mL) to 2-acetyl pyridine (6.05 g, 50 mmol). The mixture was heated under reflux for 1h, allowed to room temperature and further cooled in ice for 1 h. The obtained thick black precipitate was filtered and washed with ethanol-ether (1:9) (50 mL). The black solid is dissolved in hot methanol, a pinch of activated charcoal was added, refluxed for 5 min and filtered through celite pad to get clear yellow solution. After overnight cooling, the resulted golden yellow precipitate is filtered and dried. The golden yellow solid was recrystallized from ethanol. Yield: 9.5 g (61%).



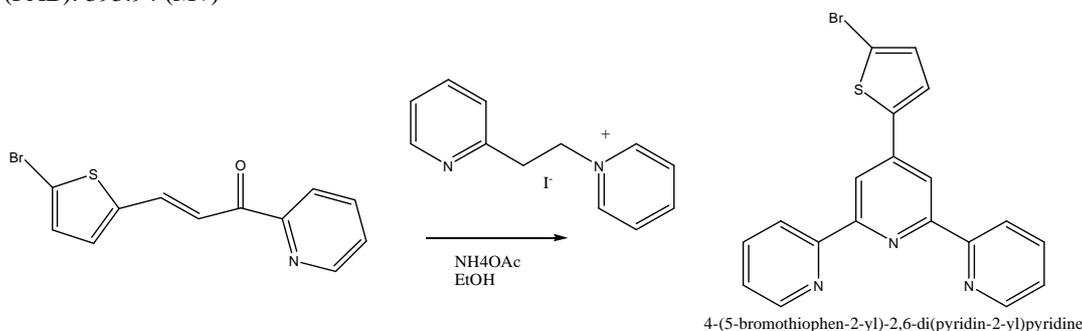
Step 3

Preparation of 4-(5-bromothiophen-2-yl)-2,6-di(pyridin-3-yl)pyridine (C)

2-(5-Bromothiophen-2-yl)-1-pyridin-2-yl-propenone (A) (1.499 g, 5 mmol), 1-(2-oxo-2-pyridin-2-yl-ethyl) pyridinium iodide (B) (1.69 g, 5 mmol), ammonium acetate (5.0 g) and ethanol (50 mL) were heated under reflux for 14 h. The resulted precipitate was collected by filtration and purified by column chromatography employing hexane, dichloromethane and ethyl acetate as eluents. The compound was found to be a colourless powder.

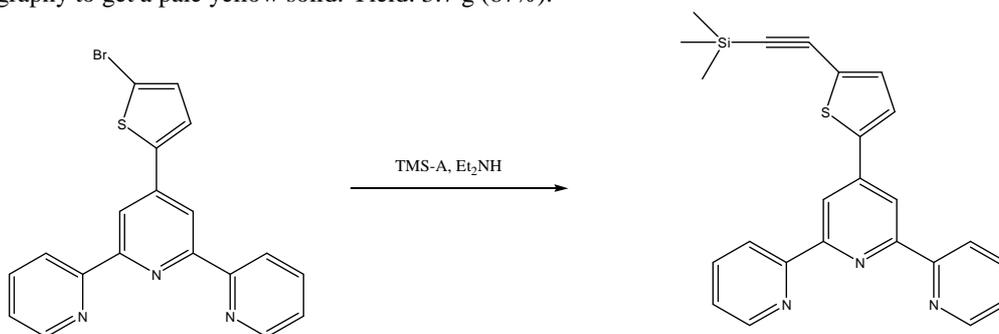
Yield: 2.0 g (41%).

Mass: (FAB): 393.94 (M⁺)



Step 4**Preparation of 4-(5-(2-(Trimethylsilyl)ethynyl)thiophen-2-yl)-2,6-di(pyridin-3-yl)pyridine (D)**

4-(5-Bromothiophen-2-yl)-2,6-di(pyridin-3-yl)pyridine (3.94 g, 10 mmol), Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol), CuI (20 mg, 0.1 mmol), triphenyl phosphine (104 mg, 0.4 mmol), trimethyl silyl acetylene (1.18 g, 12 mmol) and diethyl amine (50 mL) were charged into a flask sequentially under nitrogen and refluxed for 12 h. The volatiles removed under vacuum then the resulting solid was extracted in diethyl ether. Organic layer was washed with brine solution, dried over anhydrous MgSO₄ and evaporated to leave pale yellow viscous oil. It was further purified by column chromatography to get a pale yellow solid. Yield: 3.7 g (87%).

**Step 5****Preparation of 4-(5-ethynylthiophen-2-yl)-2,6-di(pyridin-3-yl)pyridine (E)**

The yellow obtained from step 4 was almost quantitatively converted into 4-(5-ethynylthiophen-2-yl)-2,6-di(pyridin-3-yl)pyridine by stirring with methanolic sodium carbonate at room temperature for 4 h. The product was further purified by column chromatography.

Yield: 96%; Mass (FAB): 340.16 (M⁺)

**Step 6****a) Preparation of 4-(5-R₁-ethynyl-thienyl)-[2,2';6',2'']-terpyridines (F) [F1, F2, F3]**

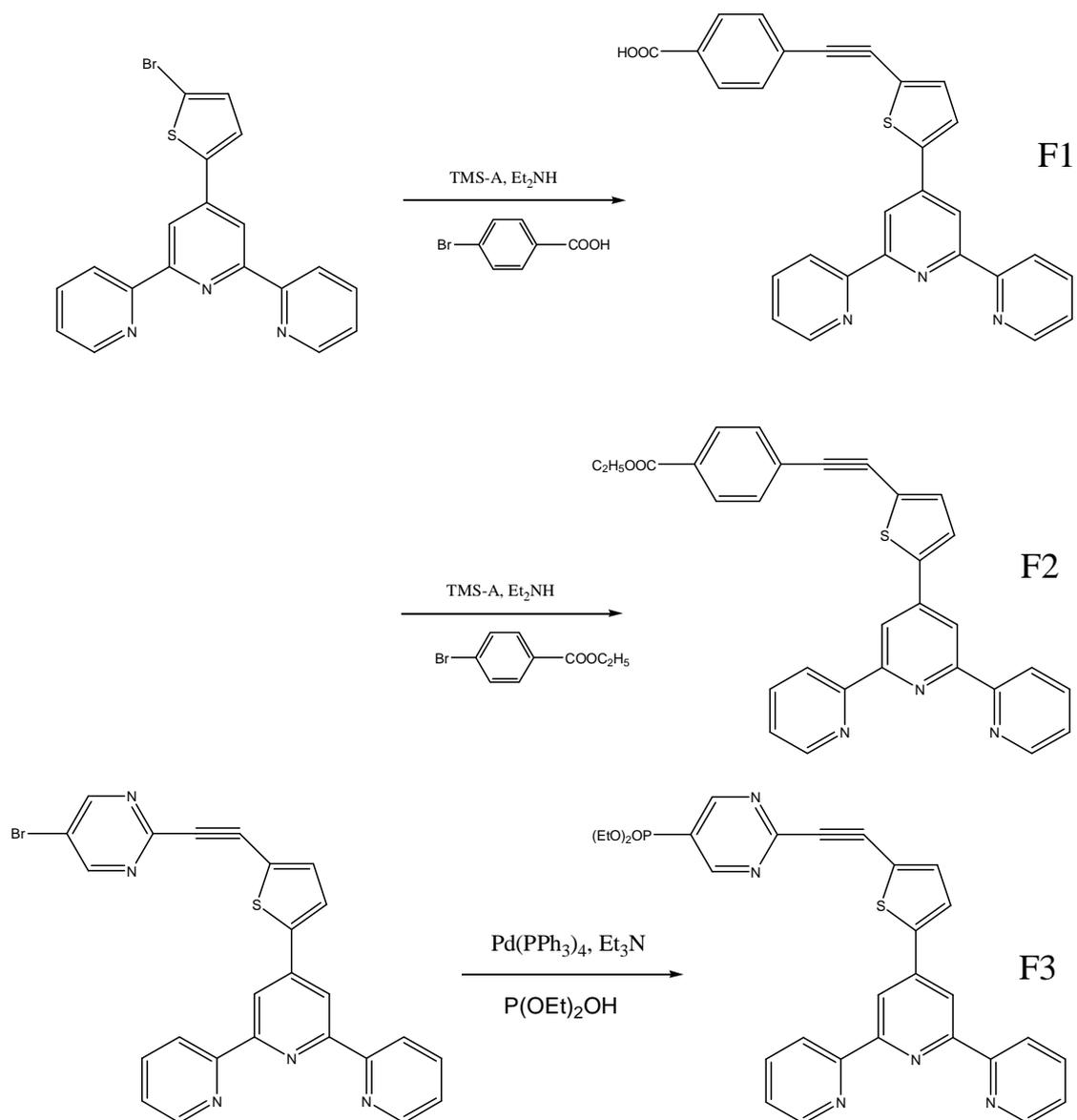
4-(5-ethynyl-thienyl)-[2,2';6',2'']-terpyridine (E) (3.94 g, 10 mmol), Pd(PPh₃)₂Cl₂ (140 mg, 0.2 mmol), CuI (20 mg, 0.1 mmol), triphenyl phosphine (104 mg, 0.4 mmol), appropriate bromo- or iodo- derivative of R₁ (12 mmol) and diethyl amine (50 mL) were charged into a flask sequentially under nitrogen and refluxed for 12 h. The volatiles removed under vacuum then the resulting solid was extracted in dichloromethane. Organic layer was washed with brine solution, dried over anhydrous MgSO₄. After removal of the solvent in vacuum, it was further purified by column chromatography.

Yield: 70 - 80 %.

F1: R₁ = 4-benzoic acid

F2: R₁ = 4-ethylbenzoate

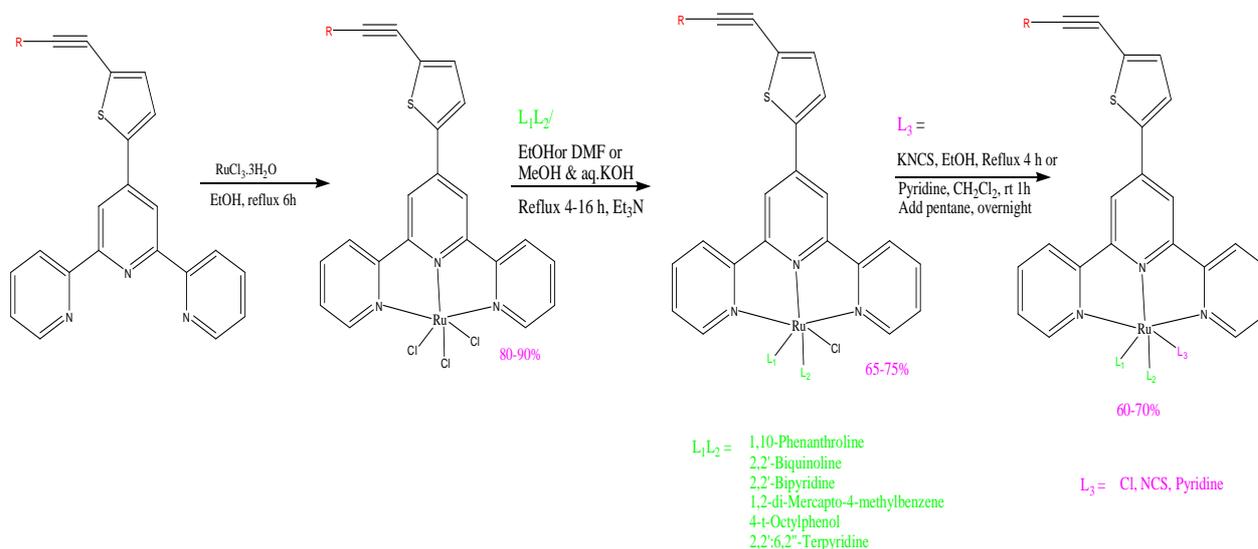
F3: R₁ = diethyl pyrimidin-5-yl-5-phosphonate



2.2. Preparation of Ruthenium Complexes

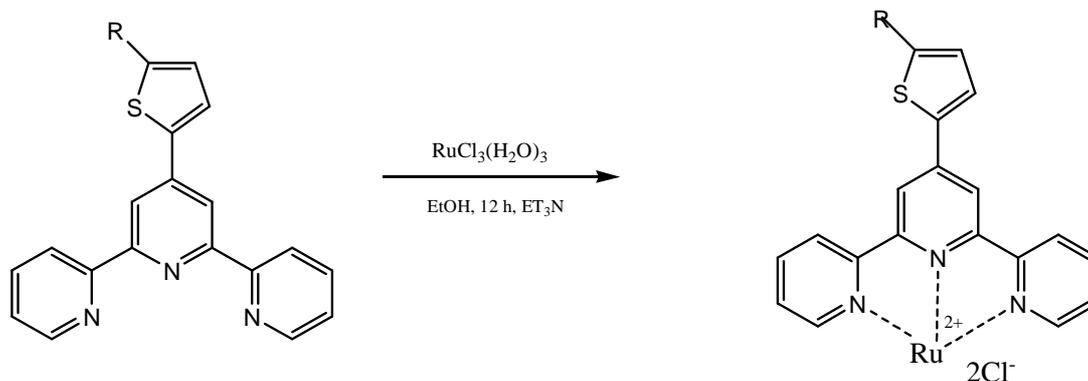
The above synthesized terpyridine ligand is then complexed with ruthenium metal to form $[Ru(tpy)Cl_3]$

Synthetic Route to Ru(II) Complexes



General Method of Preparation of Ruthenium Terpyridyl Complexes [8] $[Ru(tpy)Cl_3]$

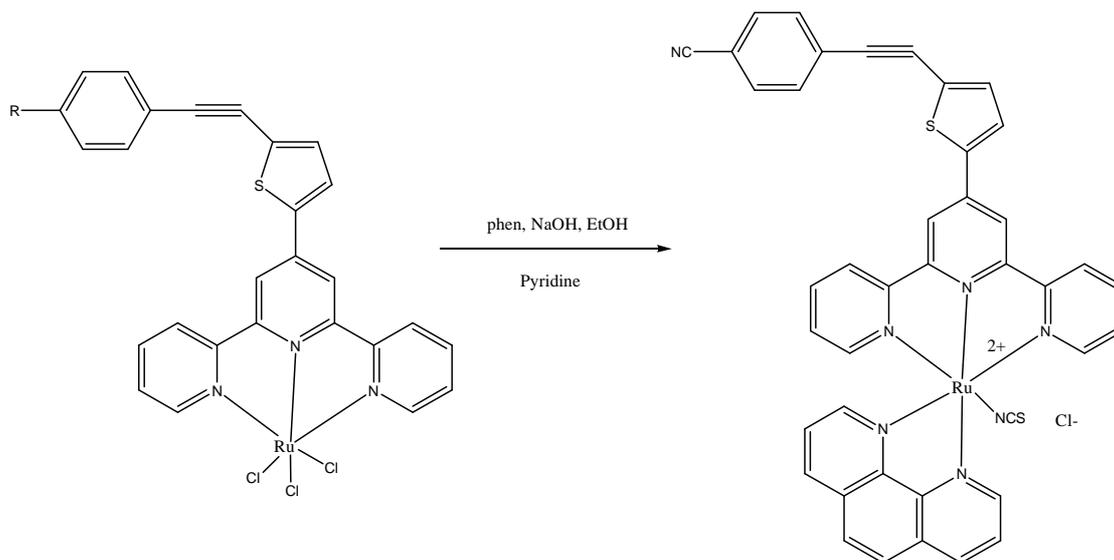
2 mmol of terpyridines (**F1**, **F2** & **F3**), 520 mg of $RuCl_3 \cdot 3H_2O$ and 100 ml of anhydrous ethanol were refluxed for 5 h under nitrogen atmosphere. The mixture was cooled, the precipitate was filtered off, washed with ethanol and diethyl ether, recrystallized in ethanol and methanol (1:1) mixture and dried in vacuum to yield about 70-90 % solid product. The complex was confirmed by mass spectra and elemental analysis.



2.3. Synthesis of Ruthenium terpyridine complex with 1,10 phenanthroline $[Ru(tpy)(phen)Cl] Cl$ [9]

Preparation of Ruthenium(II) complexes containing substituted thienylterpyridines (tpy) and 1,10-phenanthroline (phen) $[Ru(tpy)(phen)Cl]Cl$ [9]

0.5 mmol of $[Ru(tpy)Cl_3]$, 101 mg (0.51 mmol) of phen. H_2O and 50 ml ethanol were subjected to reflux for 16 h under nitrogen atmosphere followed by addition of 1 ml triethylamine which served as reductant and stirred for 1 hr at room temperature. Then solution was concentrated by removing 60 % solvent by using rotavapor. The resulting purple solid was filtered off, washed with cold water, cold ethanol and diethyl ether. The compound was further recrystallized in ethanol or purified by short silica gel column with EtOH, MeCN and DMF as eluents.



2.4. Characterisation analysis

Routine mass spectra and elemental analyses were obtained using in-house facilities of Institute of Chemistry, Academia Sinica, Taipei, Taiwan. The starting materials were prepared and purified by literature methods.

Cyclic voltammetry experiments were performed using a fully automated HCH Instruments electrochemical analyzer and a three electrode set-up consisting of a glassy carbon working electrode, a platinum wire counter electrode, and an SCE reference electrode. All experiments were performed in dry CH_3CN containing tetra-*N*-butylammonium tetrafluoroborate (0.2 mol dm^{-3}) as the background electrolyte. Absorption spectra were recorded with a Hitachi U3310 spectrophotometer, while corrected luminescence spectra were recorded with a Hitachi F4500 spectrophotometer.

RESULTS AND DISCUSSION

Characterization was made on the basis of UV spectroscopy, elemental analysis, mass spectrometry and cyclic voltammetry

3.1. Mass, UV spectroscopy & Elemental analysis

Mass and UV Spectral Data of $[\text{Ru}(\text{tpy})(\text{phen})\text{Cl}]\text{Cl}$

Table 1.1

Mass	UV (nm)	$\epsilon_{\text{max}} (\lambda_{\text{max}})$
863(863) (FAB)	227, 267, 325, 530, 782	1725 (502), 7375(530)

*Theoretical values in parenthesis

3.2. Elemental analysis of $[\text{Ru}(\text{tpy})(\text{phen})\text{Cl}]\text{Cl}$

Table 1.2

C	H	N
59.67(59.89)	3.31(3.39)	9.65(9.75)

*Theoretical values in parenthesis

The absorption spectrum recorded for Ruthenium complex in dilute butyronitrile solution as given in table 1.1 exhibits an intense (formally) spin-allowed, metal-to-ligand charge-transfer (MLCT) transition centered at 480-520nm. There is a fairly intense tail on the low-energy side that stretches as far as 580-620nm and can be attributed to the spin-forbidden MLCT absorption transitions.

On the higher energy side, the thiophene-substituted terpyridine ligand absorbs between 300 and 350 nm, while the unsubstituted terpyridine ligand shows an absorption band at 280 nm. The MLCT region is assumed to contain contributions arising from electron injection into both parent and substituted ligands. Weak phosphorescence can be detected in deoxygenated solution at room temperature for Ruthenium complex. This peak is relatively narrow and is centered at 700-730nm. The corrected excitation spectrum shows good agreement with the absorption spectrum and the emission profile remains independent of excitation wavelength.

The energy-minimized structure of Ru complex and confirms the expected pseudo-octahedral geometry around the metal center. The thiophene ring appears to lie coplanar with the attached terpyridine ligand in an orientation that maximizes orbital overlap throughout the ligand. However, there is only a small barrier to rotation around the acetylene bond.

3.3. Cyclic voltammetry

Cyclic Voltammetric Data of $[Ru(tpy)(phen)Cl]Cl$

Table 1.3

Reduction Potential E_{red} (mV)#	Oxidation Potential E_{ox} (mV)#	$E_{ox}(Ru^{+2/+3})$ Vs Ag/Ag+ (mV)
-1439, -1187, +181	-1159, +537	+800 (98)

*Ferrocene used as standard. #Values include Fc peaks

Cyclic voltammetry data as given in the table 1.3 showed that the metal center undergoes a quasi-reversible, one-electron oxidation process with a half-wave potential ($E_{1/2}$) of 1.33V versus Ag/AgCl. Two successive quasi-reversible, one-electron reduction processes are found with $E_{1/2}$ values of -1.11v and -1.43 v versus Ag/AgCl, respectively. Comparison to related complexes [10,11,12] indicates that the first reduction step corresponds to addition of an electron to the ethynylated terpyridine ligand. The second reductive process is due to electron attachment to the unsubstituted terpyridine. That this latter reduction is much easier than for the parent complex, $[Ru(tpy)_2]^{2+}$ ($E_{1/2}$) -1.25 V and -1.52V vs Ag/AgCl is probably attributable to partial electron delocalization over the ethynylene group, reducing electrostatic factors. It is also clear that the large difference in $E_{1/2}$ values will localize the added electron at the substituted ligand. Oxidation of the metal center in Ru complex occurs at the same potential as for the parent complex [2]

CONCLUSION

The reported ruthenium complexes have wide absorption bands with high and low energy radiation from sun. It ranges from 400nm to 800nm as evidenced by the table 1.1. Solar energy from this band width is available for earth's crust is about 10%. All the polypyridyl ruthenium complexes show emission at longer wavelengths since they are containing donor and acceptor moieties. With thienyl bridge will be an interesting and better ruthenium dye for TiO_2 solar cells due to their absorption and emission properties. The acceptor part with the carboxylic ester group has been well documented as the best anchoring group to transport electrons to the semiconductor surface.

The presence of moisture and protic solvent vapours, the available hydroxyl group on the surface of TiO_2 is acting as antenna to capture the carboxylic groups and forming a network. This network is supported by the ligand attached to the other side of ruthenium. Electron donating core present in the other part of ruthenium, thus forming an electron chain and continuous injection of electron. After absorption of solar radiation by ruthenium complex, electron is being injected to the conduction band of TiO_2 through the network. The continuous flow of conduction band electrons of TiO_2 is subsequently responsible for electrical energy storage. This phenomenon can also be used for construction of other photovoltaics such as LEDs, LCDs and data encryption devices employing ruthenium complexes.

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