

Synthesis, photophysical and electrochemical studies of N,N-bis(3,5-dimethylpyrazol-1-yl-methyl)-heterocyclic-bipyridine-thiocyanato-ruthenium(II) complexes



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Introduction



- Ruthenium occupies the central position of the d-block transition metal [1]
- It readily forms coordinate complexes with different derivatives [2].
- The basic interest in chemistry of ruthenium is due to part of the electron transfer properties exhibited by the complexes of the metal [2].
- Variation of the coordination environment around ruthenium play a key role in modulating the redox properties of the complexes [2].



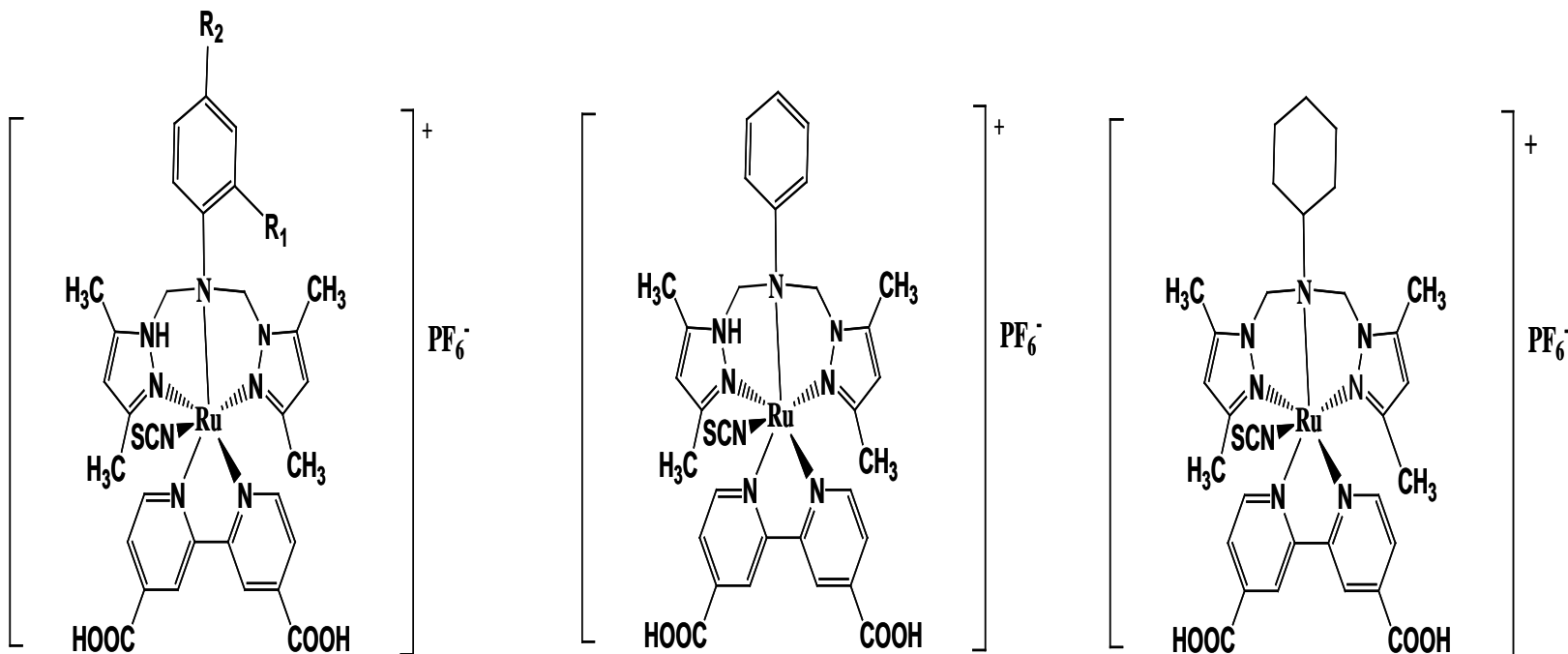
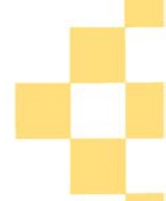
Ruthenium(II) Complexes



- Ruthenium(II) complexes utilization currently takes special interests on technologies that exploit photophysical/electrochemical properties in areas such as photoredox catalysis, cellular imaging, organic-light emitting diodes and Dye-sensitized solar cells (DSSCs [1])
- The major advantages of ruthenium complexes in electrochemical applications centres on relatively low MLCT energy [2]. The MLCT involves the electron transfer from d-orbital of the metal centre to π^* orbital of ligand [3].
- Ruthenium(II) complexes with nitrogen containing heterocyclic ligands are widely studied due to their intensive ability to absorb visible and near UV-light [4].



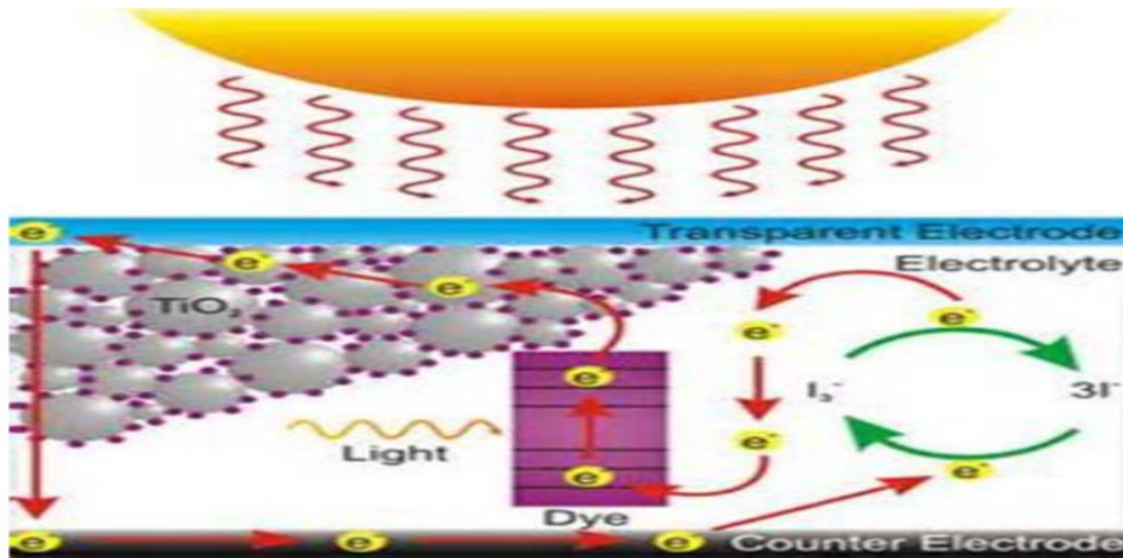
Ruthenium(II) complexes containing N-heterocyclic ligands



- Rational design and choice of N,N-bis(3,5-dimethylpyrazol-1-yl-methyl)-heterocyclic ligands is to enhanced the photophysical and electrochemical properties of ruthenium(II) complexes as potential sensitizers for dye sensitized solar cells.



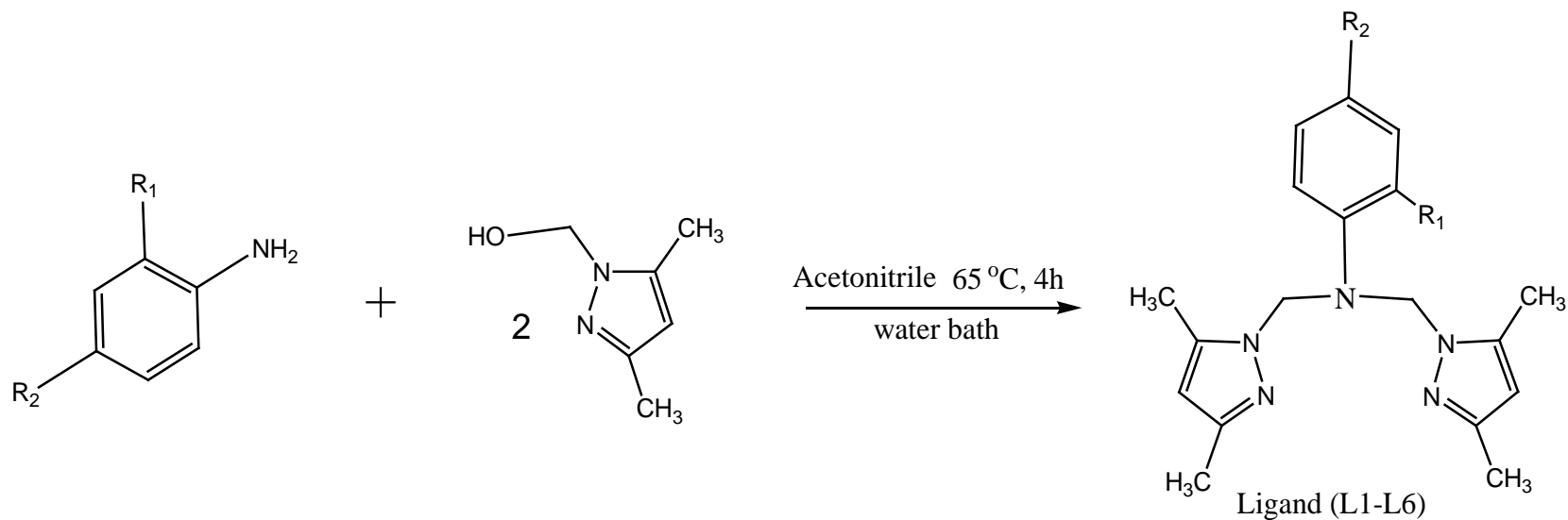
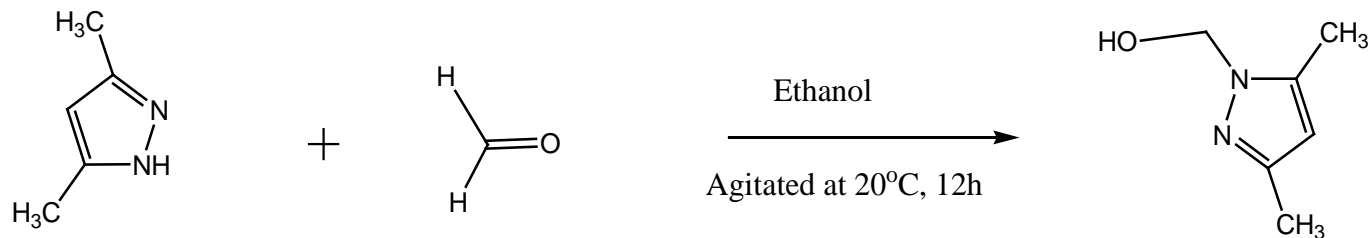
Dye Sensitized Solar Cell



- The high solar-to-electrical energy conversion efficiency of dye-sensitized solar cell is majorly anchored on the synthesis of efficient light capturing dye sensitizers usually transition metal complexes presenting broad and strong metal-to-ligand transfer (MLCT) absorption and incorporating functional groups [5,6].
- Major emphasis has been given to nitrogen heterocyclic ligands which are capable of complexing with different metal ion such as Ru(II) [6].



Preparation of Pyrazolic tripod Derivatives (L1-L6)

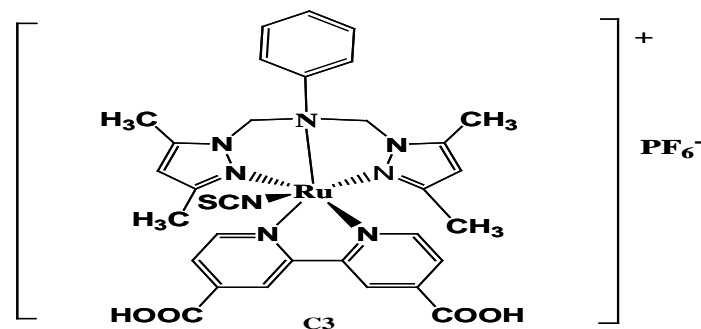
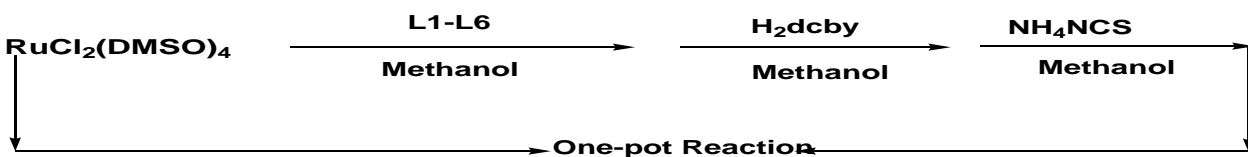
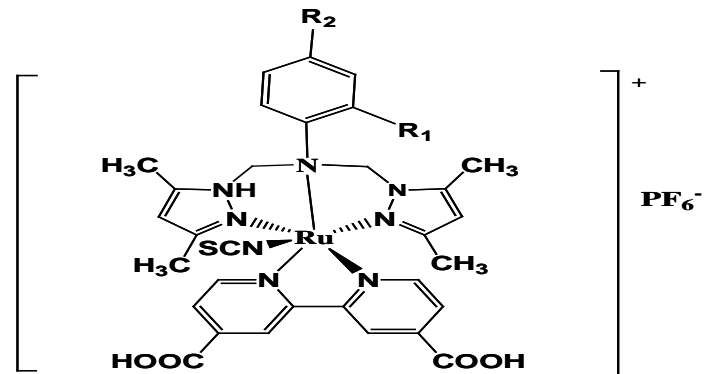


Synthetic Approach: Heterocyclic ruthenium(II) complexes

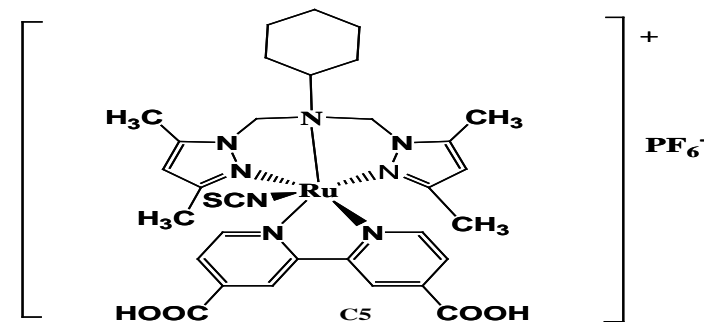


$R_1 = \text{COOH}$ for L1 and NO_2 for L2

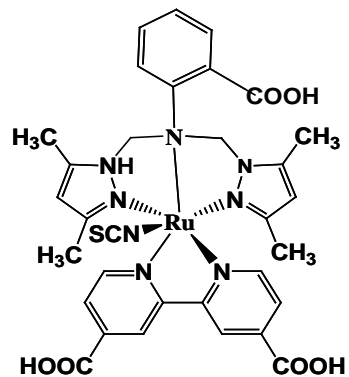
$R_2 = \text{OCH}_3$ for L2, L6 and CH_3 for L4



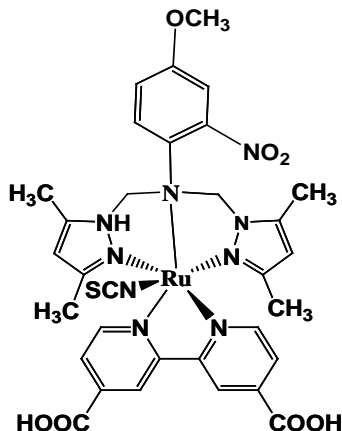
OR



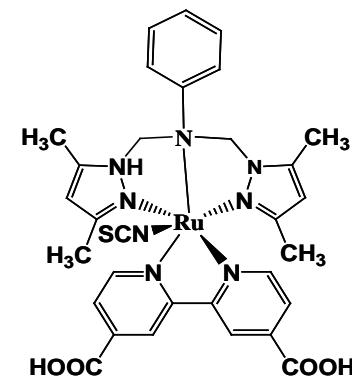
N,N-heterocyclic ruthenium(II) complexes



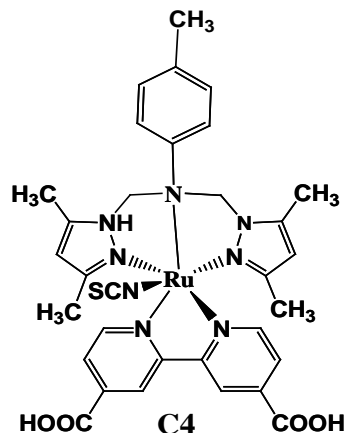
C1



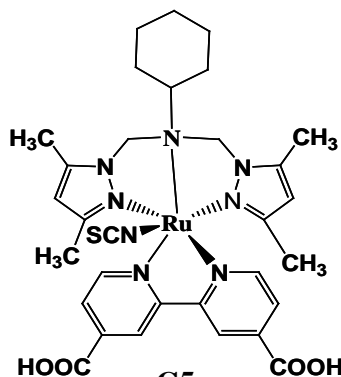
C2



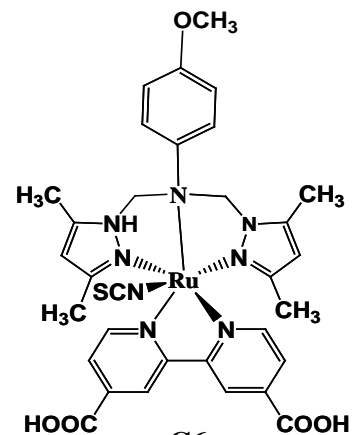
C3



C4



C5



C6

FTIR Results



Table 1. Relevant FTIR spectroscopic data (cm^{-1}) of complexes (**C1-C6**)

Complexes	$\nu(\text{O-H})$	$\nu(\text{N=C})$	$\nu(\text{C=O})$	$\nu(\text{C=S})$	$\nu(\text{M-N})$
C1	3452	2100	1718	771	446
C2	3487	2116	1722	776	432
C3	3445	2118	1734	773	446
C4	3466	2117	1731	770	446
C5	3438	2106	1727	773	439
C6	3452	2116	1731	772	432

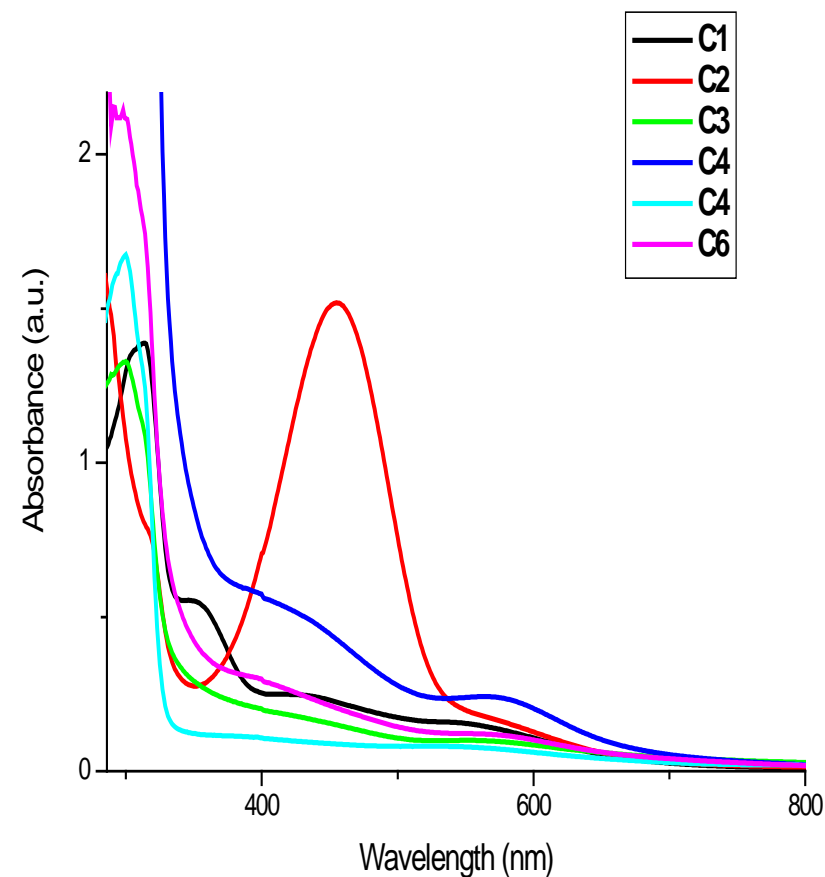


Light Harvesting-UV-Vis Results

Table 2. Absorption spectral data of complexes (C1-C6)

Complexes	Absorption λ_{max}/nm	
	$\pi-\pi^*$ band	MLCT band
C1	309	355 455, 573, 626
C2	292, 316	454, 587, 629
C3	300	432, 590, 629
C4	297	411, 585, 629
C5	299	390, 553, 620
C6	301	405, 508. 629

Measured in DMSO solution

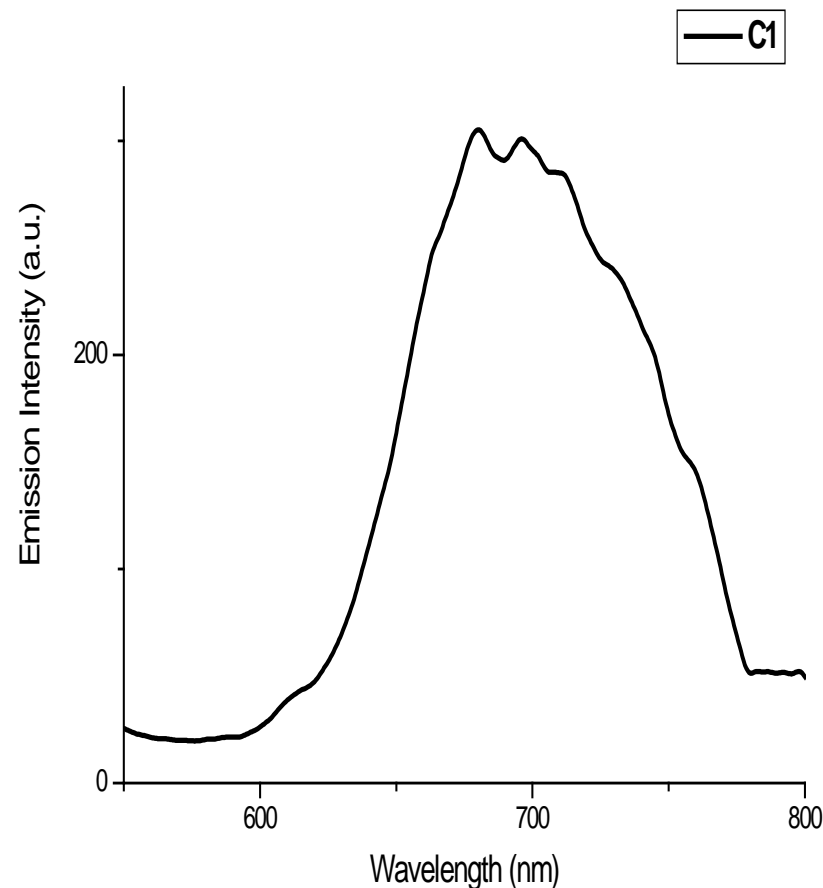


- C2 has high absorption due to NO_2 electron-drawing substituent

Emission results



- Complex (**C1**) exhibits luminescence at 695 nm when excited at 455 nm in DMSO at 295K.
- **C1** emission is ascribed to electron-withdrawing substituent of COOH on [*N,N*-bis(3,5-dimethylpyrazol-1-yl-methyl)-heterocyclic ring which is similar to ruthenium sensitizers as reported in literature. [7]



Cyclic and Square voltammetry results of C4

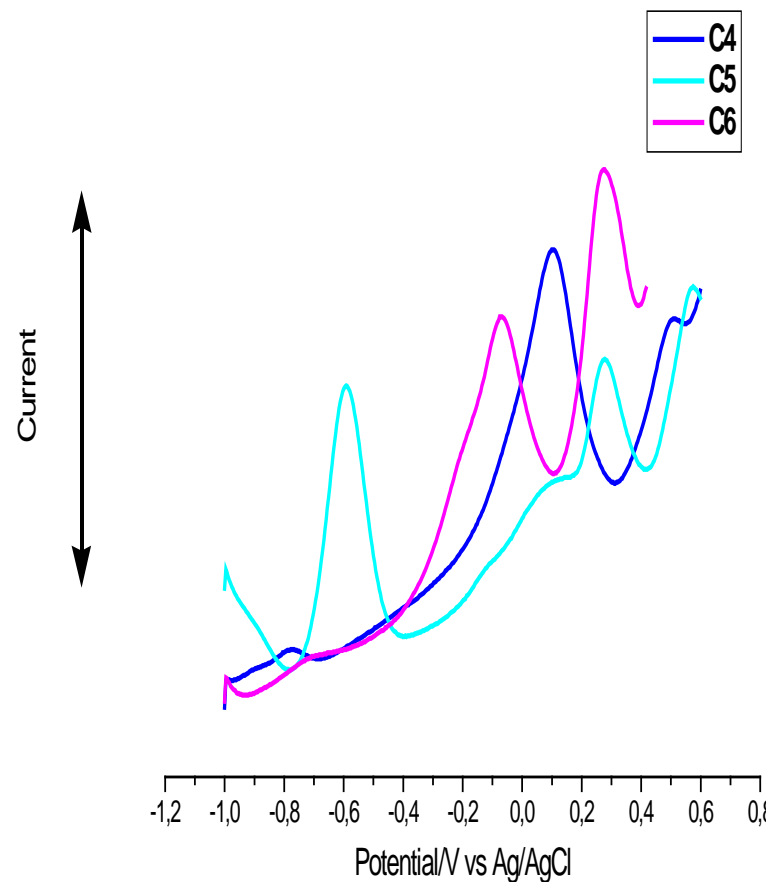
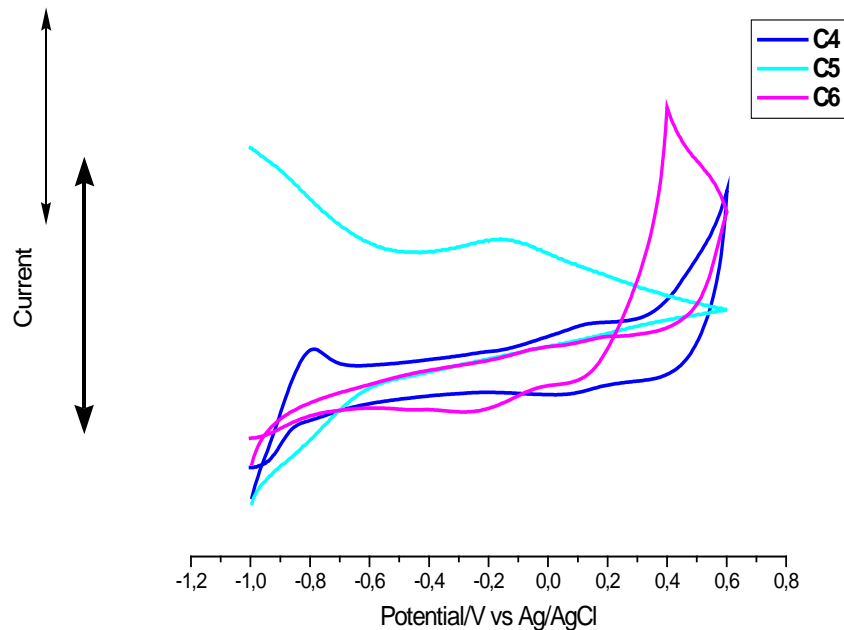


Table 3: Cyclic voltammetric data of complexes (C4-C6)

Complexes	Ru(II/III)	E_{anodic}/V	E_{cathodic}/V	$E_{1/2}/V$
C4	0.53	0.10	-0.76	-
C5	0.75	0.50	-0.97	0.13
C6	0.53	0.10	-1.10	-0.75



Summary



- Six (6) new $[\text{Ru}(\text{L1-L6})(\text{H}_2\text{dcbpy})(\text{NCS})]^+$ heteroleptic ruthenium(II) complexes containing heterocyclic ligands synthesized
- The use of heterocyclic ligands provided electron withdrawing groups (EWG) and electron donating groups (EDG) for controlling absorption, emission wavelength and redox properties
- The broad and very high intensity MLCT absorption bands make these dyes very useful for harvesting and transforming less energetic photons thereby showing its importance for photosensitization process.
- The heterocyclic ligands together with overall structure of the complexes enhanced its photophysical and electrochemical properties



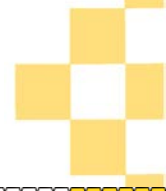


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