

**A Comparative Study of Ru (II) Cyclometallated Versus Thiocyanated Heteroleptic Complexes: Thermodynamic Force for Efficient Dye Regeneration in Dye-sensitized Solar Cells and How Low Could it Be?**

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## **1. Supporting Information and Experimental Section**

### ***Materials.***

The solvents and chemicals were either purchased from Sigma-Aldrich, Fisher Scientific or TCI-America or used as received. Sephadex LH-20 was purchased from Fisher Scientific.

### ***1.1. Analytical Measurements.***

#### ***1.1.1 UV-Vis Spectra***

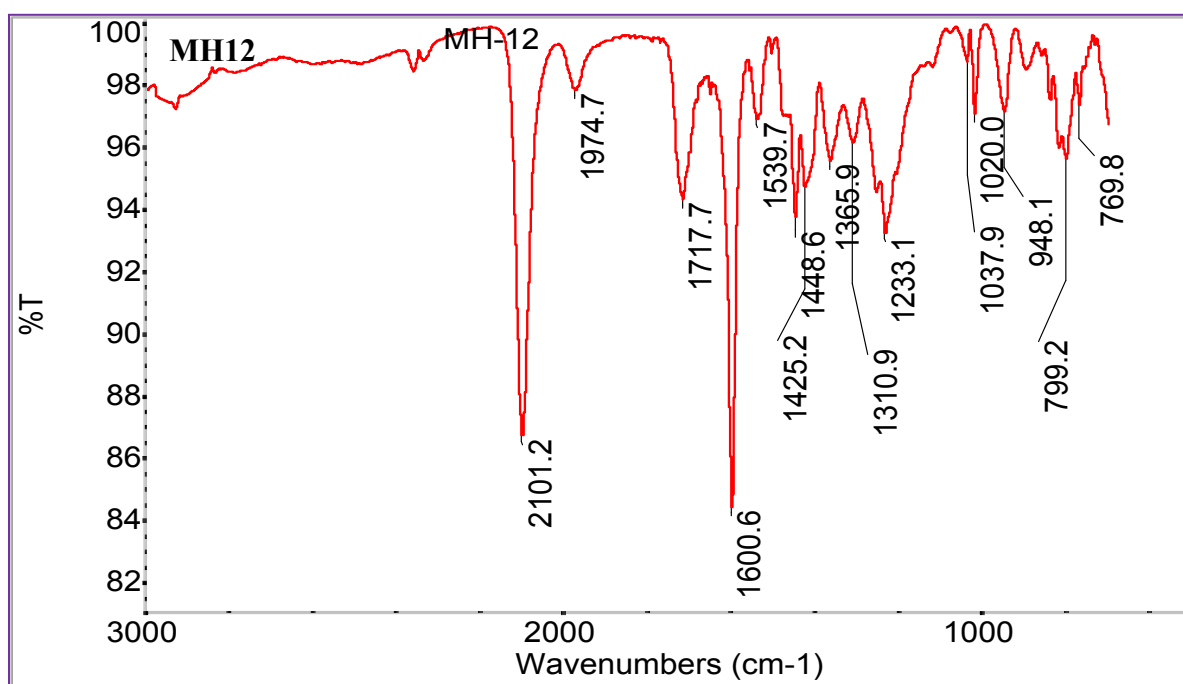
UV-Vis spectra were recorded in a 1cm path length quartz cell on a Cary 3 Spectrophotometer. A dimethylformamide solution of each complex of  $2 \times 10^{-5}$  M was prepared, and the absorbance was measured and extinction coefficient was calculated for each dye.

### 1.1.2. Fluorescence Spectra

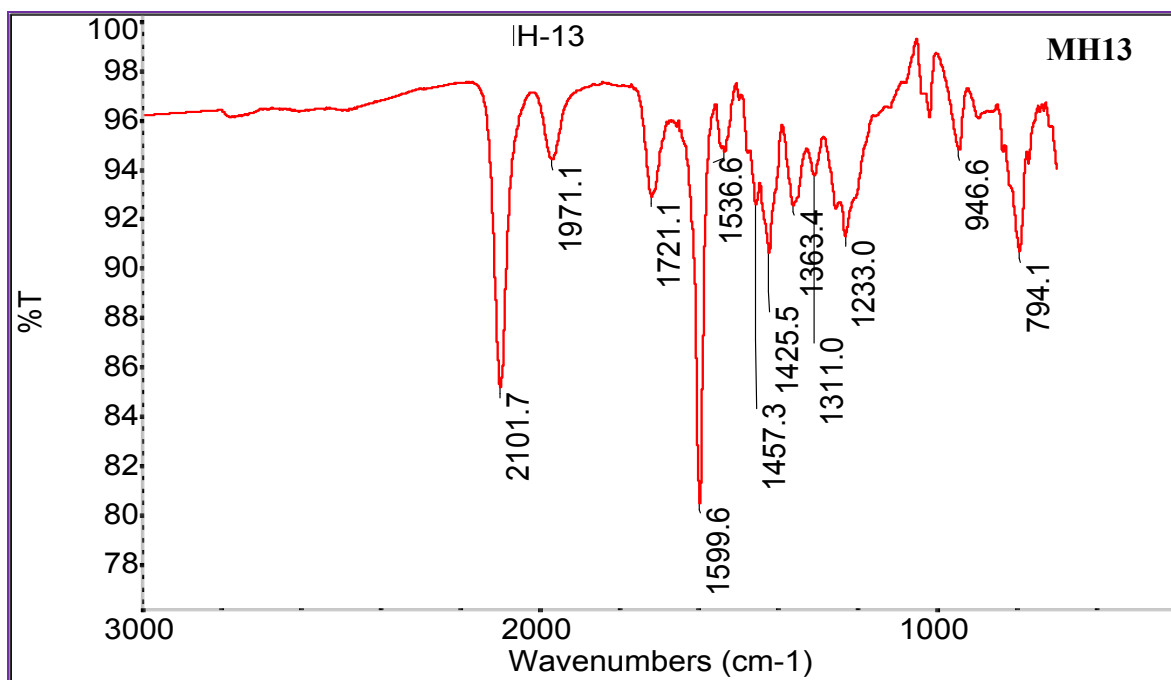
Fluorescence spectra were recorded in a 1cm path length quartz cell using  $2 \times 10^{-5}$ M solutions on a Fluorolog-311. The emitted light was detected in the steady state mode using Hamamatsu R2658 detector. The emission was measured in the steady state mode by exciting at the  $\lambda_{\text{max}}$  (lower energy MLCT band) for each dye with exit and entrance slits set at 2nm.

### 1.1.3. Attenuated Total Reflectance Fourier-transform Infra Red Spectroscopy

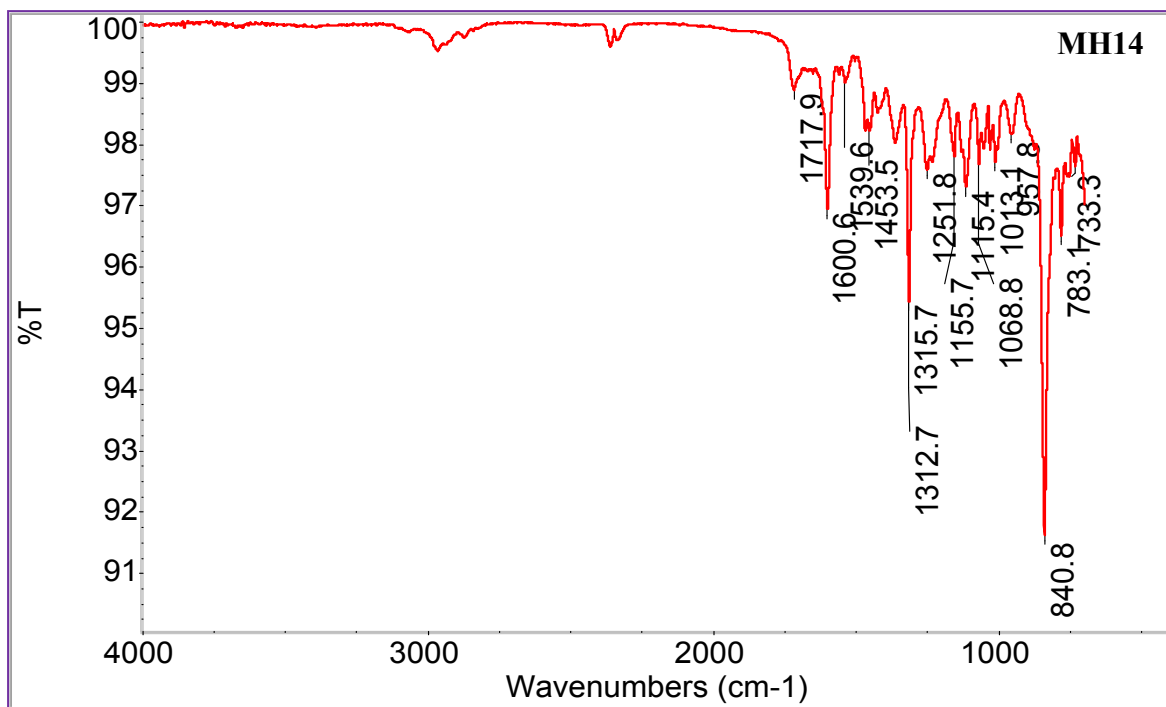
Attenuated Total Reflectance-Fourier Transform Infra Red (ATR/FT-IR) spectra were recorded on a Thermo Nicolet, Nexus 470 FTIR Spectrophotometer with Omnic 7.2 software. The compound under investigation was placed in its powder form on a germanium crystal and a pressure probe was placed in position to apply consistent pressure on the sample. An average of 32 scans was used at a resolution of  $4 \text{ cm}^{-1}$ . The complexes and intermediates were characterized using the same parameters. Figures 1S-4S, shows the FT-IR of **MH12-15** in the pure form, respectively.



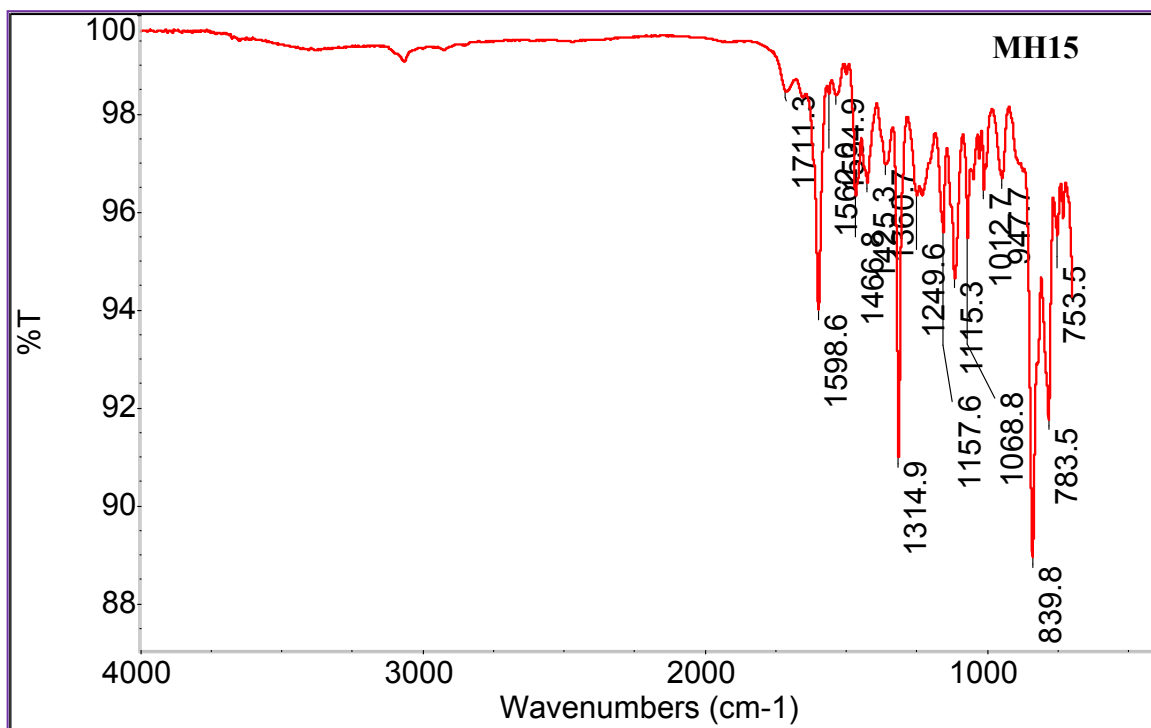
**Figure 1S** ATR/FT-IR of MH12.



**Figure 2S** ATR/FT-IR of MH13.



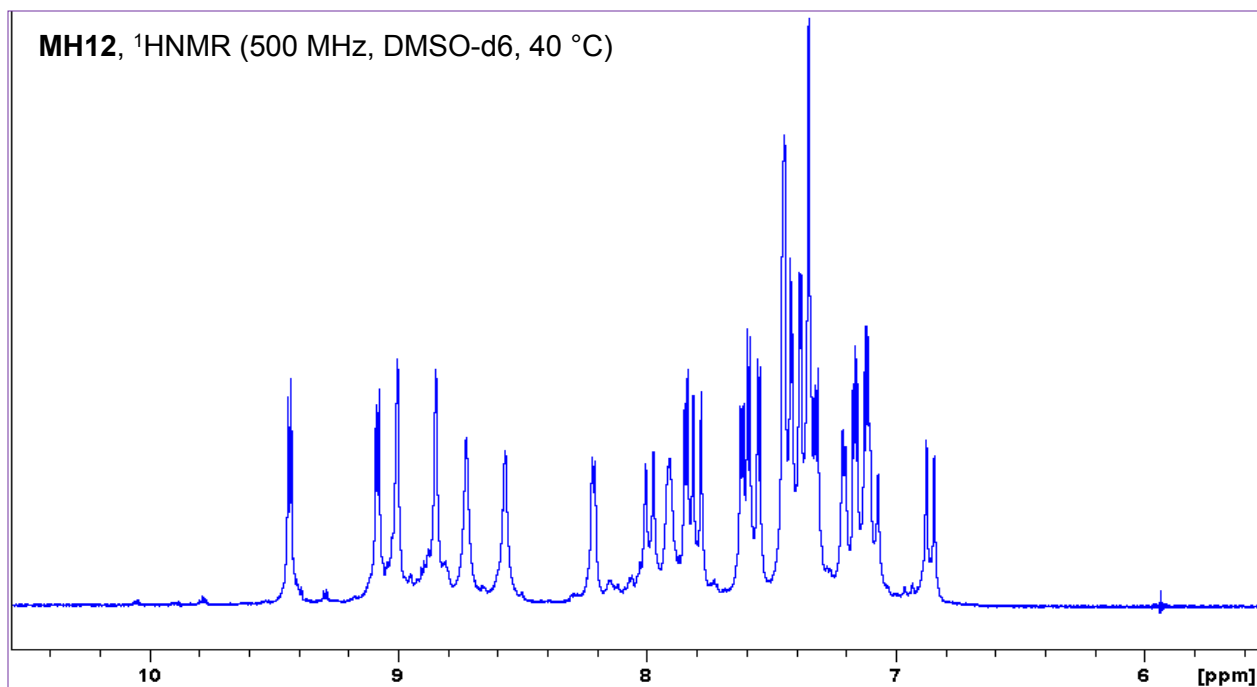
**Figure 3S** ATR/FT-IR of MH14.



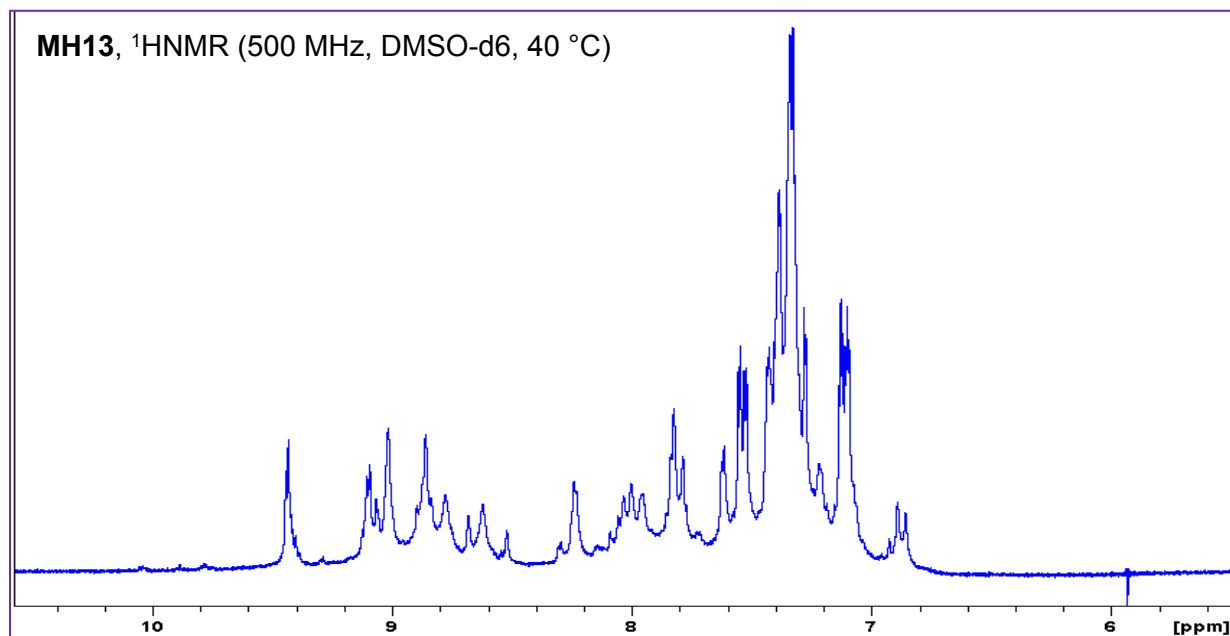
**Figure 4S** ATR/FT-IR of MH15

### 1.1.5. <sup>1</sup>H-NMR Experiments

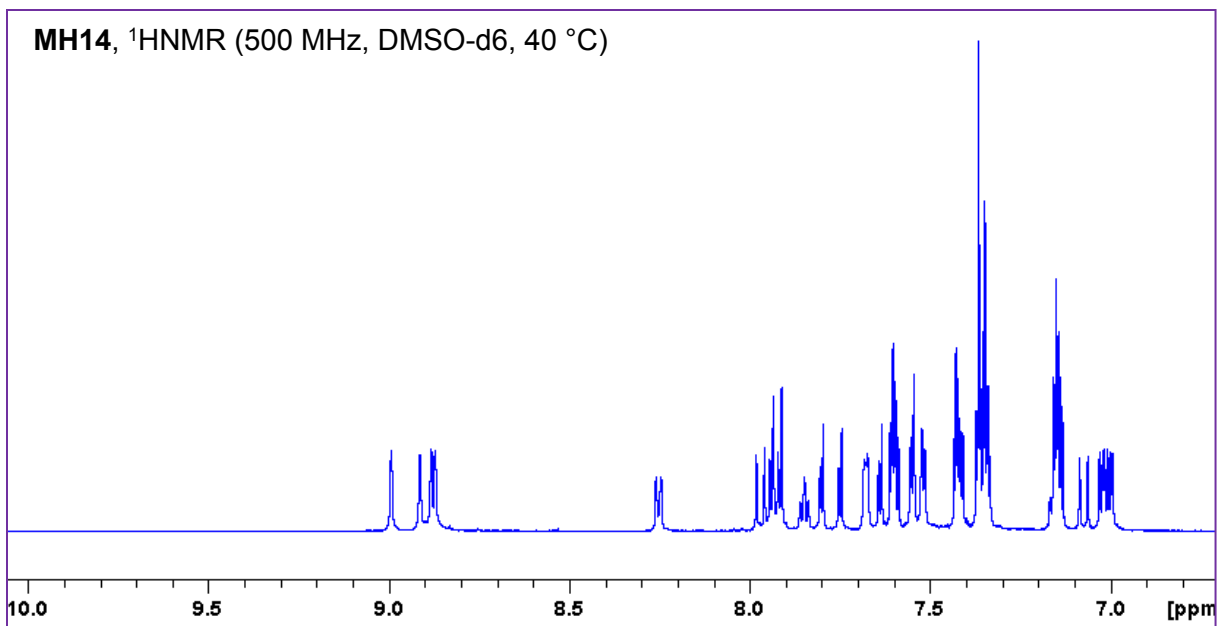
<sup>1</sup>H-NMR experiments were recorded on a Bruker 500 MHz spectrometer at 40 °C using deuterated DMSO-d<sub>6</sub> as a solvent. Splitting patterns reported here are: s (singlet), d (doublet), dd, (double-of-doublet), t (triplet), p (pentet), and m (multiplet). Chemical shifts ( $\delta$ ) and coupling constants (J) are reported in ppm and Hertz (Hz), respectively. The aliphatic range 0-5ppm is not shown for brevity. Figures 5S-8S show the H-NMR for **MH12-15**, respectively.



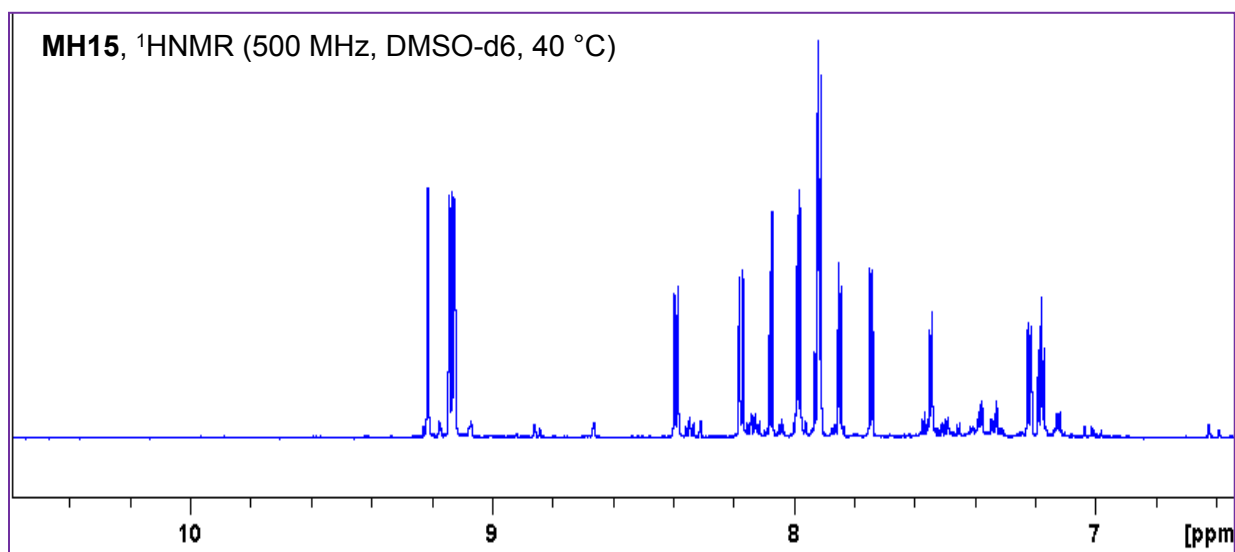
**Figure 5S**  $^1\text{H-NMR}$  of **MH12**.



**Figure 7S**  $^1\text{H-NMR}$  of **MH13**.



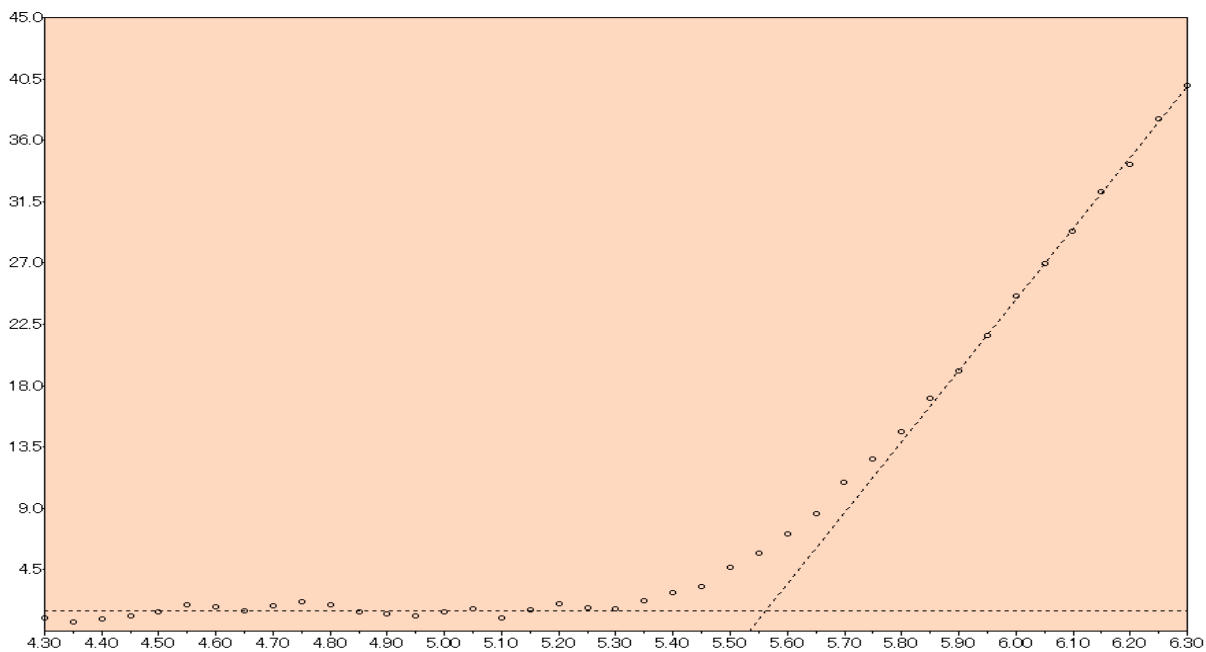
**Figure 6S**  $^1\text{H-NMR}$  of **MH14**.



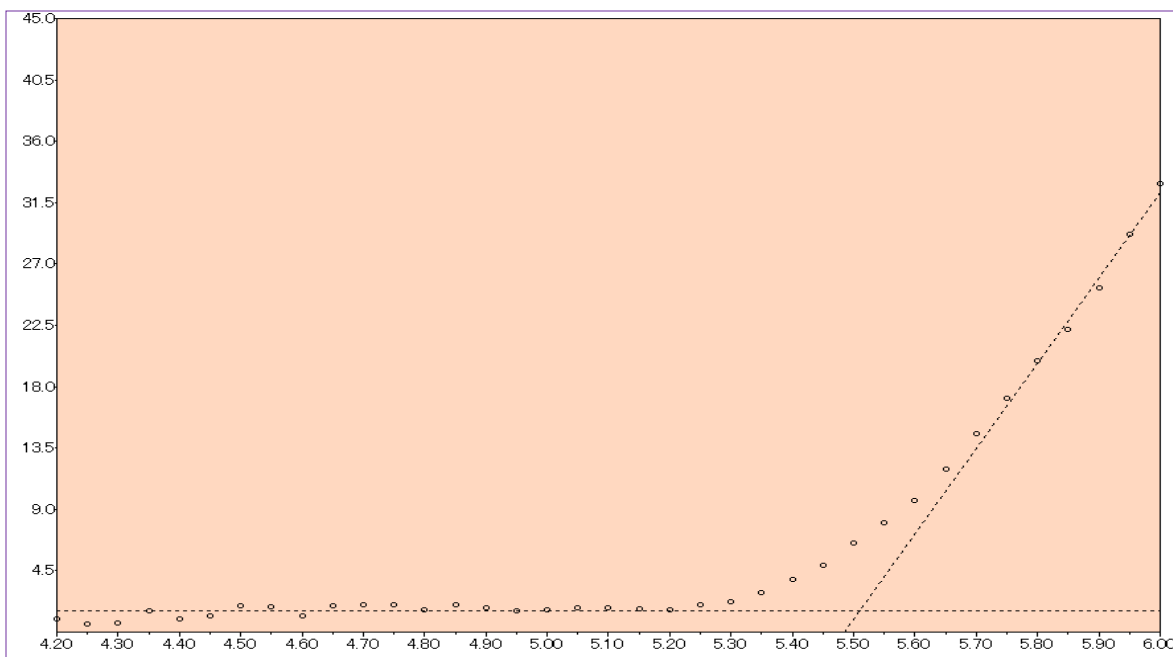
**Figure 8S**  $^1\text{H-NMR}$  of **MH15**.

### 1.1.6. Photoemission Yield Spectrometer (AC3) and $E_{0-0}$ Measurements

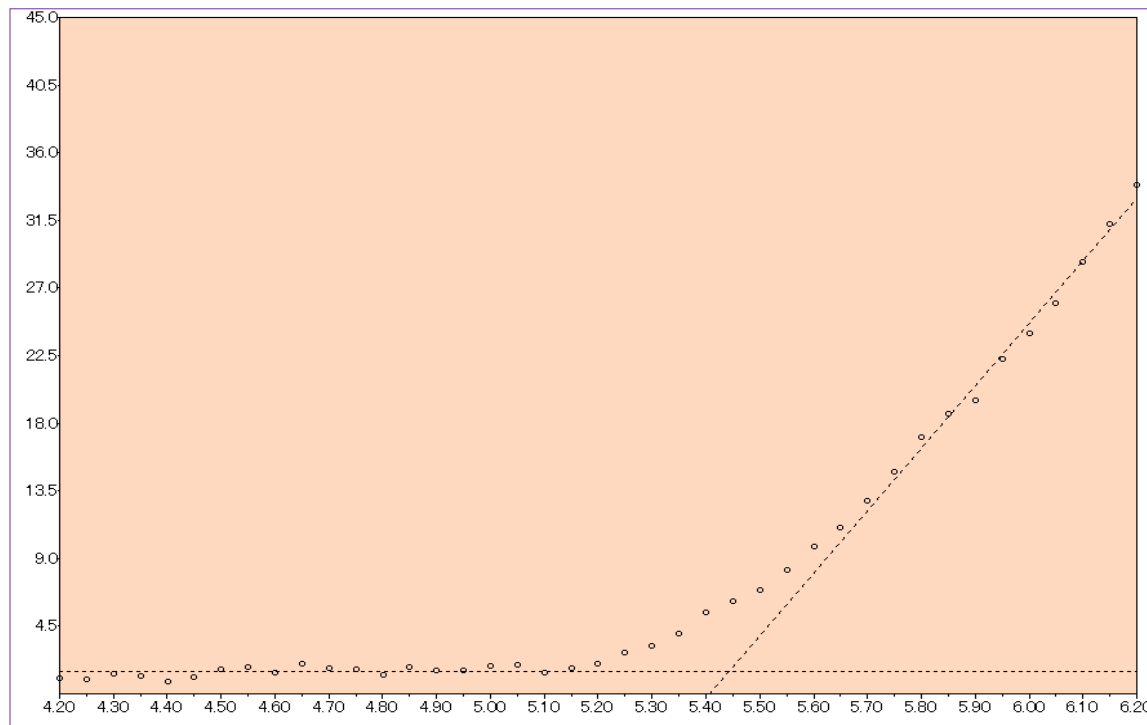
The experimental HOMO and  $E_{0-0}$  energy values for **MH12-15** and **N719** were measured using a photoemission yield spectrometer and the experimental absorption/emission spectra point of overlap, respectively, and the procedure was described in detail elsewhere [4]. Figures 9S-12S show the HOMO energies of **MH12-15**, respectively.



**Figure 9S** HOMO energy (-5.56eV) of **MH12**.

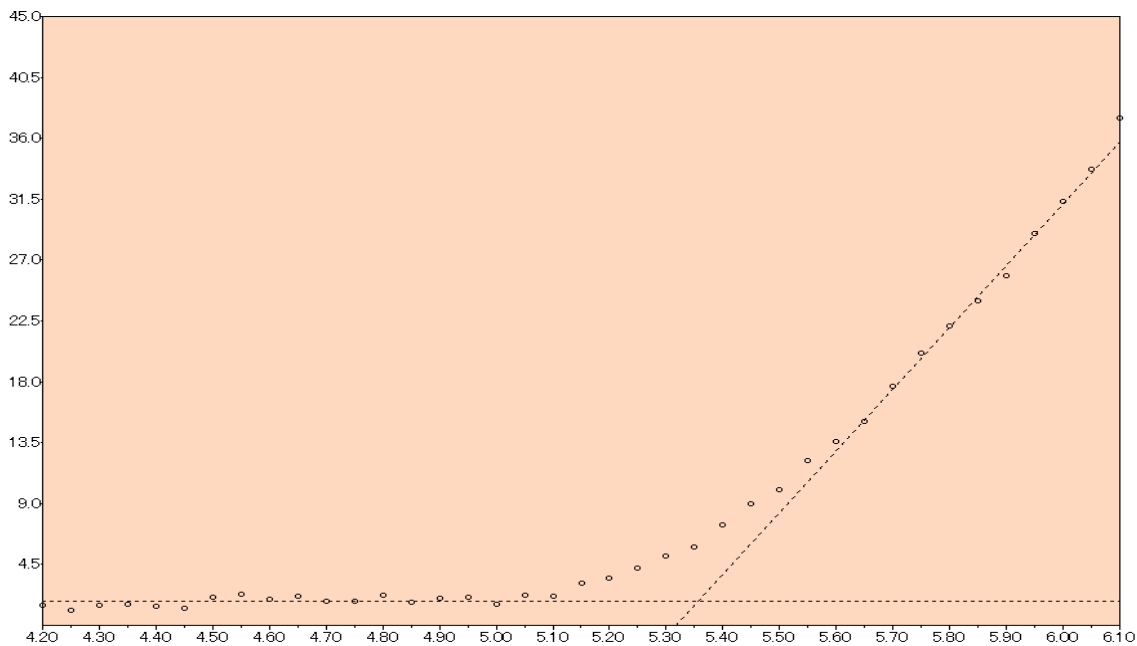


**Figure 10S** HOMO energy (-5.51eV) of **MH13**.



**Figure 11S** HOMO energy (-5.44eV) of **MH13**.





**Figure 12S** HOMO energy (-5.36eV) of MH15.

### 1. 2. 1. TiO<sub>2</sub> Electrode Preparation

A double-layer TiO<sub>2</sub> photoelectrode (10+5) μm in thickness with a 10 μm thick nanoporous layer and a 5 μm thick scattering layer (area: 0.25 cm<sup>2</sup>) were prepared using a reported method [1]. Fluorine doped tin oxide-coated glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8-10 ohm<sup>-2</sup> and an optical transmission of greater than 80% in the visible range were screen printed using anatase TiO<sub>2</sub> colloids (particle size ~13nm) obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). Nanocrystalline TiO<sub>2</sub> thin films were deposited onto the conducting glass by screen-printing which was then sintered at 500 °C for 1 hour. The film thickness was measured with a Surfcom 1400A surface profiler (Tokyo Seimitsu Co. Ltd.). The electrodes were impregnated with a 0.05 M titanium tetrachloride solution and sintered at 500 °C. The films were further treated with 0.1M HCl aqueous solutions before examination [2]. The dye solutions (2 × 10<sup>-4</sup> M) were prepared in 1:1:1 acetonitrile, *tert*-butyl alcohol and DMSO. Deoxycholic acid was added to the dye solution as a coadsorbent at a concentration of 20 mM.

The electrodes were immersed in the dye solutions and then kept at 25 °C for 20 hours to adsorb the dye onto the TiO<sub>2</sub> surface.

### **1.2.2. Fabrication of Dye-Sensitized Solar Cell.**

Photovoltaic and IPCE measurements were made on sandwich cells, which were prepared using TiO<sub>2</sub> coated working electrodes and platinum coated counter electrodes, and were sealed using a 40 µm Syrlin spacer through heating of the polymer frame. The redox electrolyte consisted of a solution of 0.6 M DMPII, 0.05 M I<sub>2</sub>, 0.1 M LiI and 0.3-0.5 M TBP in acetonitrile.

### **1.2.3. Photoelectrochemical Measurements**

#### **1.2.3.1. Photovoltaic measurements**

Photovoltaic measurements of sealed cells were made by illuminating the cell through the conducting glass from the anode side with a solar simulator (WXS-155S-10) at AM 1.5 illuminations (light intensities: 100 mW cm<sup>-2</sup>).

#### **1.2.3.2. Incident Photon to Current Efficiency (IPCE) Conversion**

IPCE measurements were made on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). IPCE at each wavelength was calculated using Equation 2, where  $I_{SC}$  is the short-circuit photocurrent density (mAcm<sup>-2</sup>) under monochromatic irradiation,  $q$  is the elementary charge,  $\lambda$  is the wavelength of incident radiation in nm and  $P_0$  is the incident radiative flux in Wm<sup>-2</sup> [3].

$$IPCE(\lambda) = 1240 \left( \frac{I_{SC}}{q\lambda P_0} \right) \quad \text{Equation 2}$$

The incident photon-to-current conversion efficiency was plotted as a function of wavelength.

### 1.3.1. Synthesis of Ligands

#### 1.3.1.1 4,4'-Bis-(2-[2,2']bithiophenyl-5-yl-vinyl)-[2,2']bipyridinyl

A 100 ml pressure tube was charged with a magnetic stirrer bar, 100 mL of anhydrous DMF, 4,4'-dimethyl-2,2'- bipyridine (1.000g,  $5.428 \times 10^{-3}$  mol) and [2,2']Bithiophenyl-5-carbaldehyde (2.1088g,  $1.085 \times 10^{-2}$  mol, 5% excess was used to drive the reaction to completion), and three equivalent of  $\text{Si}(\text{CH}_3)_3\text{Cl}$ . The reaction temperature was raised to 100 °C and allowed to run for 48 hours with continuous stirring. At the end of the reaction, the solvent was removed using rotary evaporator, and the product was recovered by addition of water and filtration under vacuum to furnish the antenna ligand in 91% yield, which was used for the next step after washing with toluene. The other 4,4'-Bis-(2-[2,2';5',2'']terthiophen-5-yl-vinyl)-[2,2']bipyridinyl ligand was prepared using same procedure with a 95% yield.

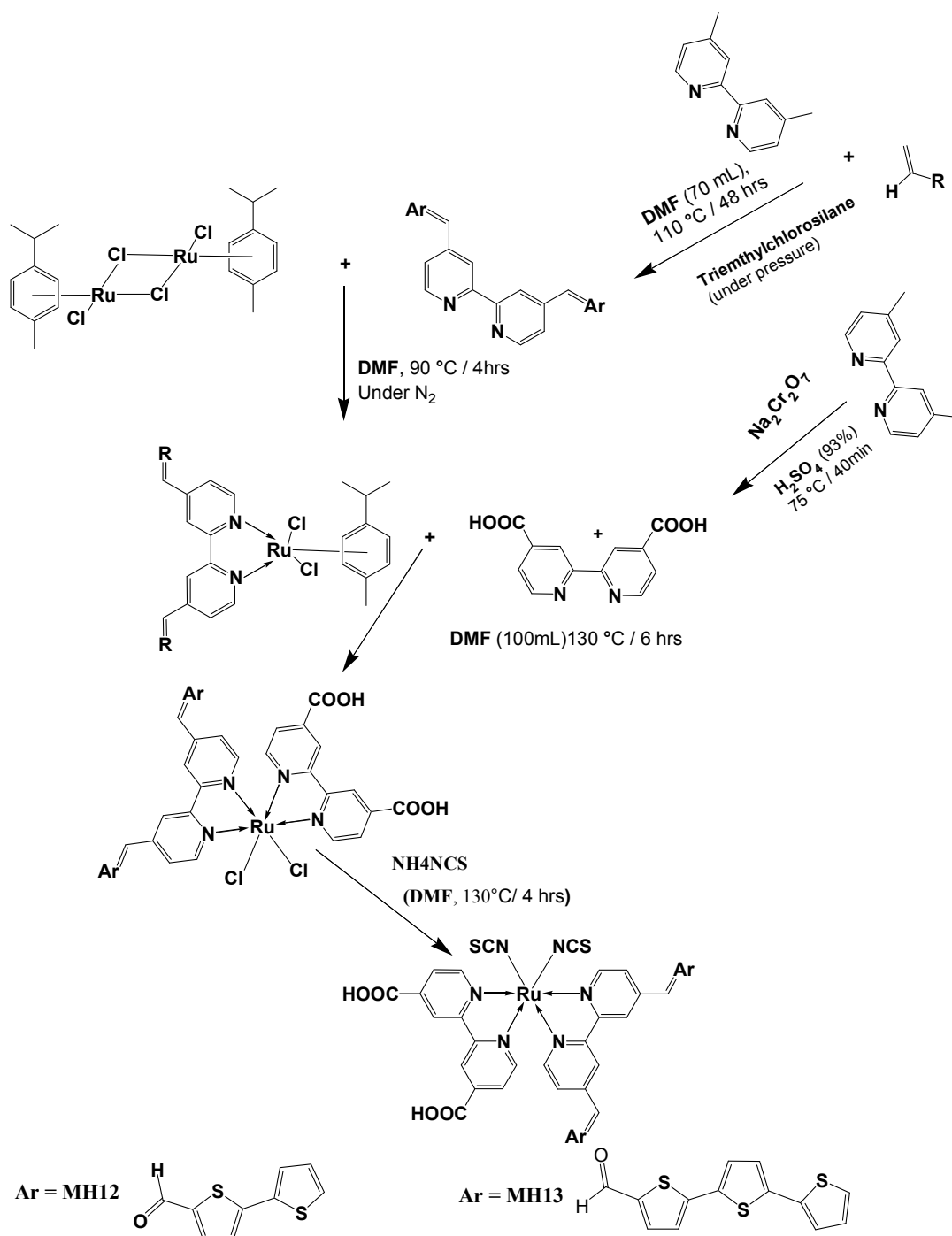
#### 1.3.1.2 Synthesis of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid

2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid was synthesized in 95% yield according to a previously reported procedure [5]

#### 1.3.1.3 Synthesis of complexes MH12 and MH13

The synthesis of MH12 was carried out in a one-pot three-step reaction. The reactions were carried out in a 250 ml reaction flask equipped with a condenser and magnetic stirrer bar under Argon. The flask was charged with anhydrous DMF (100mL), dichloro-(*p*-cymene)-ruthenium (II) dimer (0.30g,  $4.899 \times 10^{-4}$  mol) and 4,4'-Bis-(2-[2,2']bithiophenyl-5-yl-vinyl)-[2,2']bipyridinyl (0.5100g,  $9.797 \times 10^{-4}$  mol). The reaction mixture was stirred at 90 °C for 4h. Then, 2,2'-bipyridyl-4,4'-dicarboxylic acid was added (0.239 g,  $9.797 \times 10^{-4}$  mol) and the temperature was raised to 130°C and allowed to run for 6 hours. The reaction mixture was cooled down to room temperature and DMF was removed using a rotary evaporator. After 6hours, excess of  $\text{NH}_4\text{NCS}$  (1.00g) was added to the reaction mixture, and the reaction mixture was allowed to run for another 4h at 130°C. The reaction mixture was cooled down to room temperature and DMF was removed using a rotary evaporator. Water was added to the flask, and the insoluble solid were vacuum filtered and washed with de-ionized water and ether. The product was dried overnight to give the crude product in 92% yield, with respect to the starting

material. Complexes **MH13** were prepared using same procedure in 93% crude yield. Scheme 1 summarizes the general synthetic route for complexes **MH12** and **MH 13**.

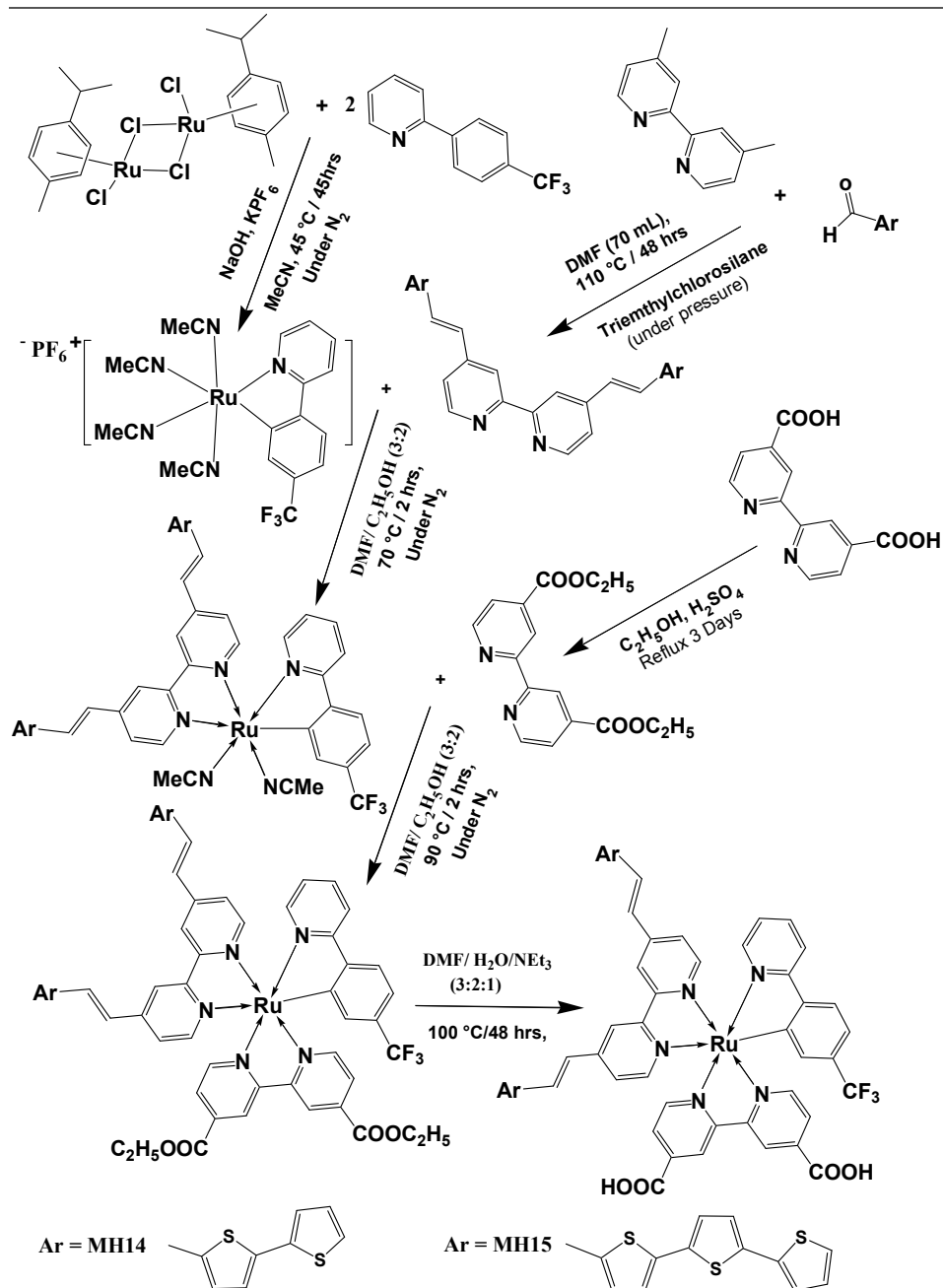


**Scheme 1** General route for the synthesis of ligands and complexes **MH12-13**.

### 1.3.1.4 Synthesis of complexes MH14 and MH15

**Ru (II) [cis(4,4'-Bis-(2-[2,2']bithiophenyl-5-yl-vinyl)-bis[2,2'] bipyridinyl-2, 2'-bipyridinyl-4, 4'-dicarboxylic-(2-(2-(4-Trifluoromethyl-phenyl)-pyridine))] (MH14)** complex were synthesized in dark under argon atmosphere. In a 250 ml reaction flask dichloro-(*p*-cymene)-ruthenium (II) dimer (0.556g,  $9.08 \times 10^{-4}$  mol) and 2-(4-Trifluoromethyl-phenyl)-pyridine (0.406g,  $1.816 \times 10^{-3}$  mol) was dissolved in 100 mL of MeCN and then NaOH (0.073g,  $1.816 \times 10^{-3}$  mol) and  $KPF_6$  (0.670g,  $3.638 \times 10^{-3}$  mol) was added to the stirring solution. The reaction mixture was stirred at 45 °C for 45h. The MeCN was removed from reaction mixture using a rotary evaporator and collected yellow-greenish product which is purified by column chromatography using silica gel as the stationary phase and mixture of  $CH_2Cl_2$  and MeCN (98:2) as the mobile phase.

In the second step a 250 mL flask was charged with  $[C^{\wedge}N]Ru(CH_3CN)_4(2-(4-Trifluoromethyl-phenyl)-pyridine)]^+PF_6^-$  (0.400g,  $6.324 \times 10^{-4}$  mol) and 4,4'-Bis-(2-[2,2']bithiophenyl-5-yl-vinyl)-[2,2']bipyridinyl (0.339g,  $6.324 \times 10^{-4}$  mol) using DMF,  $C_2H_5OH$  mixture (100 mL, 3:2). The reaction mixture was stirred for 2h at 70 °C and then increased the temperature to 90°C and added [2,2']Bipyridinyl-4,4'-dicarboxylic acid diethyl ester (0.190g,  $6.324 \times 10^{-4}$  mol) and stirred for further 2h under nitrogen. The DMF,  $C_2H_5OH$  mixture was removed from reaction mixture using a rotary evaporator. De-ionized water was added to flask and neutralized using 0.01M  $HNO_3$  to pH 7.03. The green product filtered and purified by column chromatography, using Sephadex LH-20 as the stationary phase and pure methanol as the mobile phase and collected green product. The purified product was hydrolyzed by refluxing for 48h at 100 °C in DMF,  $H_2O$  and Triethylamine (50 ml, 3:1:1) the insoluble solid were vacuum filtered and washed with de-ionized water and ether. The product was dried overnight to give 70% yield with respect to the  $[C^{\wedge}N]Ru(CH_3CN)_4(2-(4-Trifluoromethyl-phenyl)-pyridine)]^+PF_6^-$  intermediate, overall synthesis is shown in scheme 1. Complexes **MH15** were prepared using same procedure in 74% crude yield.



Scheme 2 General route for the synthesis of ligands and complexes MH14-15

### 1.3.2. Purification

**MH12-13** was purified on a column using Sephadex LH-20 as the stationary phase and pure methanol as the mobile phase. The crude dye of **MH12** was dissolved in a mixture of methanol and Tetrabutylammonium hydroxide and loaded on Sephadex LH-20, and the compound was eluted using methanol neat. The main band was collected and acidified using 0.1M HCl until the pH dropped to 3.0, and the acidified solution was kept in a refrigerator for 12 hours. Then, the precipitate was filtered, washed with plenty of de-ionized water to remove remaining HCl. The same purification procedure was repeated two times for the **MH14-15** using methanol and acetonitrile (80:20) as mobile phase in order to obtain in the pure form.

### References:

- 1- Wang, P.; Zakeeruddin, S. M.; Comte, P.; Charvet, R.; Humphry- Baker, R.; Grätzel, M. *J. Phys. Chem. B* **2003**, *107*, 14336
- 2- Wang, Z.; Yamaguchi, T.; Sugihara, H.; and Arkawa, H.; Langmuir, **2005**, *21*, 4272.
- 3- Islam, A.; Chowdhury, F. A.; Chiba, Y.; Komiya, R.; Fuke, N.; Ikeda, N.; Nozaki, K.; and Han, L.; Chem. Mater. **2006**, *18*, 5178
- 4- Islam, A.; Sugihara, H.; Singh, L. P.; Katoh, R.; Yanagida, M.; Takahashi, Y.; Murata, S.; and Arakawa, H. *Inorg. Chem.*, **2001**, *40*, 5371