Supporting Information and Experimental Section

Influence of Cyclic Versus Acyclic Oxygen-containing Electron Donor Ancillary Ligands on the Photocurrent and Photovoltage for High Efficiency Dye-sensitized Solar Cells

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Materials.

The solvents and chemicals were either purchased from Sigma-Aldrich and Fisher Scientific or TCI-America, 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 $2x10^{-5}$ 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 x 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 λ_{max} (lower energy MLCT band) for each dye with exit and entrance slits set at 10nm.

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 cm^{-1}. The complexes and intermediates were characterized using the same parameters. Figures 1S, 2S, and 3S show the FT-IR of MH01, MH03 and MH05 in the pure form, respectively.

MH01: 2102 cm^{-1} (-NCS stretch, N-bonded isomer, very strong); 1719 cm^{-1} (C=O stretch of -COOH)
MH03: 2103 cm^{-1} (-NCS stretch, N-bonded isomer, very strong); 1719 cm^{-1} (C=O stretch of -COOH)
MH05: 2101 cm^{-1} (-NCS stretch, N-bonded isomer, very strong); 1720 cm^{-1} (C=O stretch of -COOH)

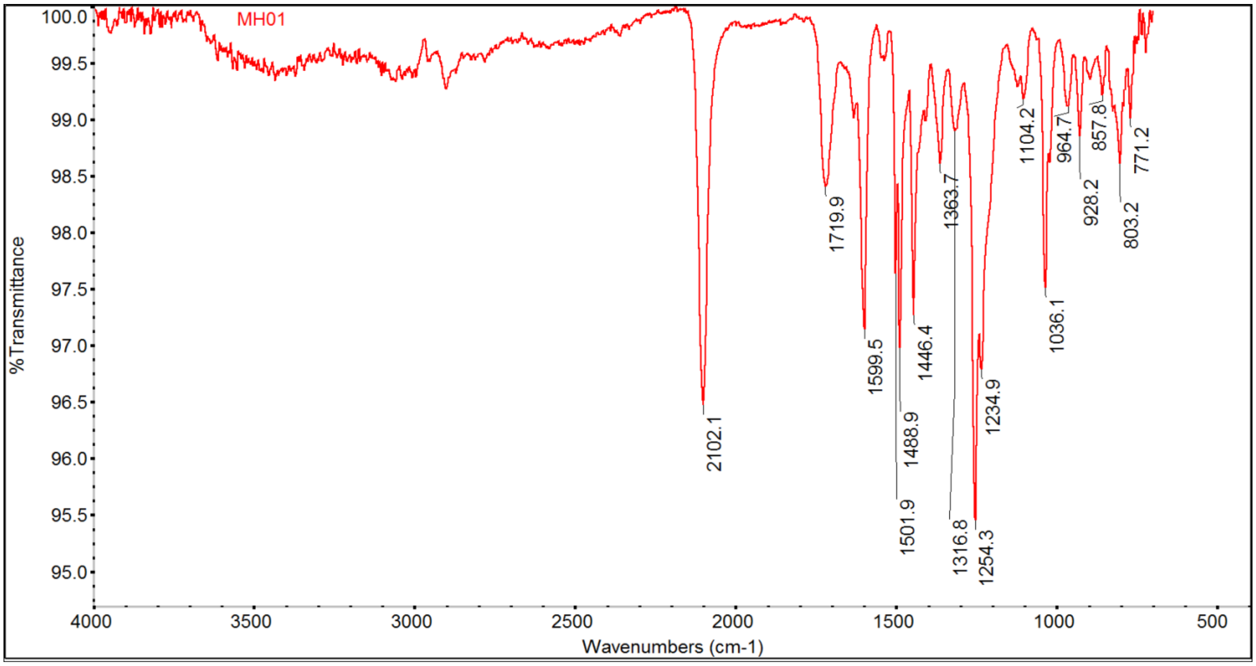

Figure 1S ATR/FT-IR of MH01.

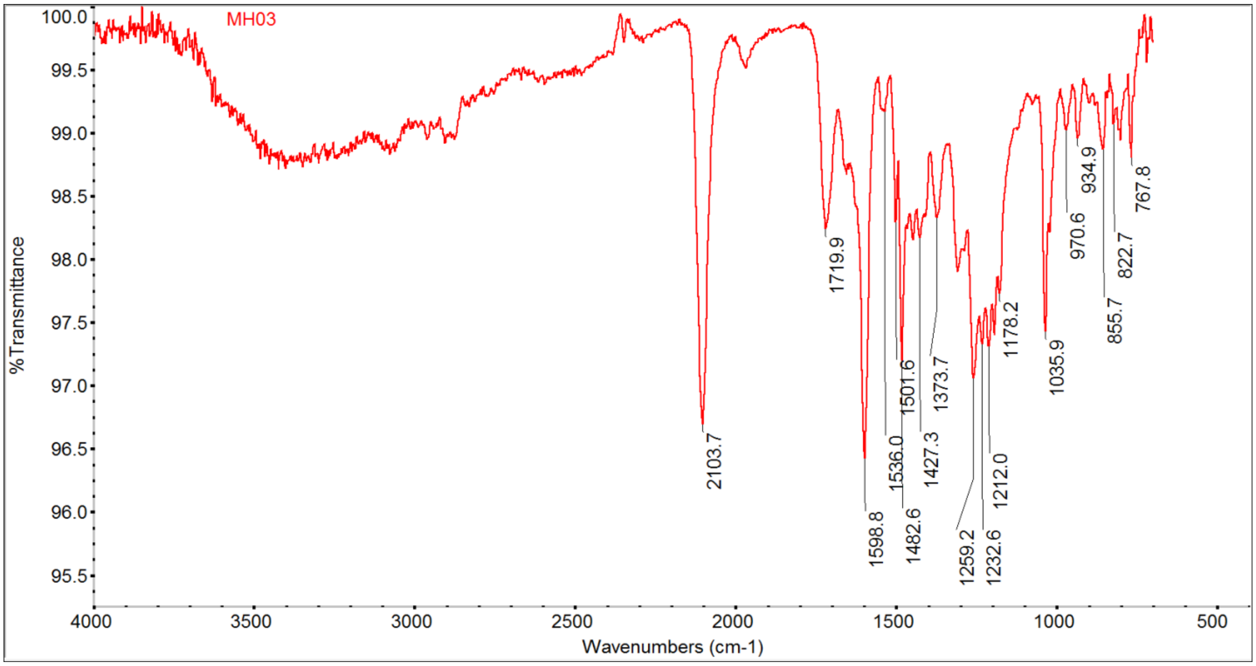

Figure 2S ATR/FT-IR of MH03.

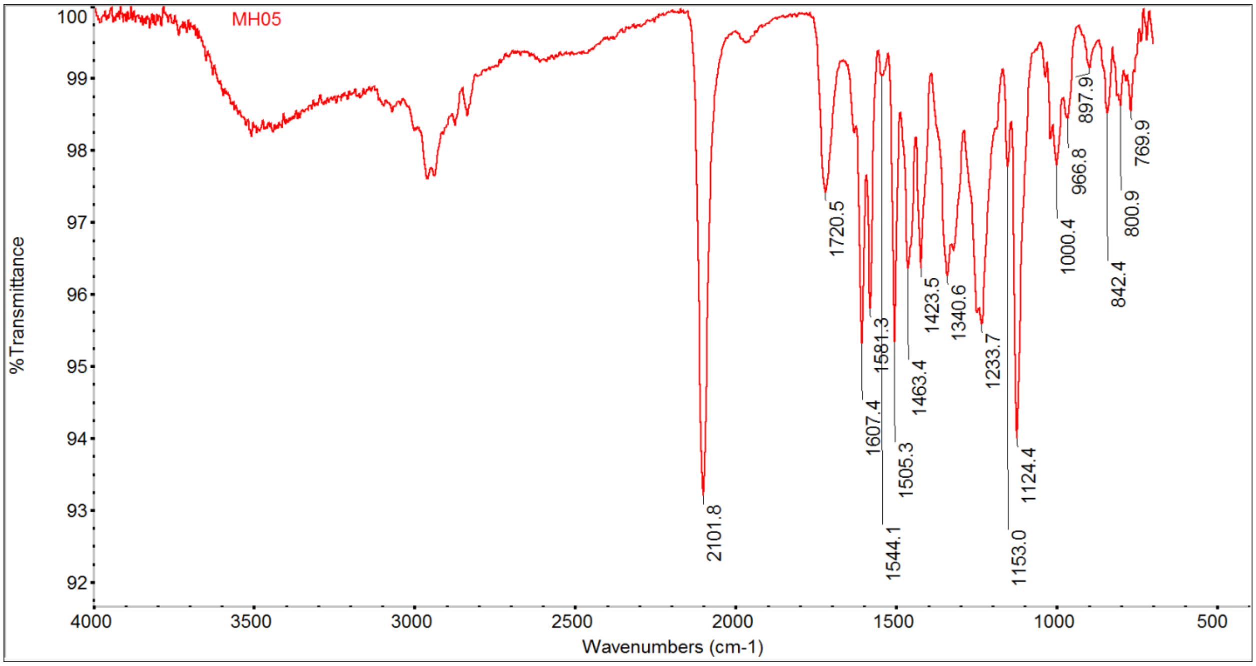

Figure 3S ATR/FT-IR of MH05.

1.1.4. Mass Spectroscopy

ESI-MS was recorded on an Agilent Technologies 6210 LC-TOF mass spectrometer in the negative ion mode. The sample was prepared in methanol in the presence of a small amount of tetrabutylammonium hydroxide (TBAOH). The fragmenter voltage was set at 220.0 V and results from 19 scans in the case of MH01, 14 scans in the case of MH02-03, 32 scans for MH04 and 22 scans in the case of MH05 were averaged. Figures 6S-10S show the -ESI-MS of MH01-04 and MH05 with one TBA per molecule, singly charged, respectively. The ESI-MS patterns shown in Figures 4S-6S are the pattern of ruthenium isotopes.

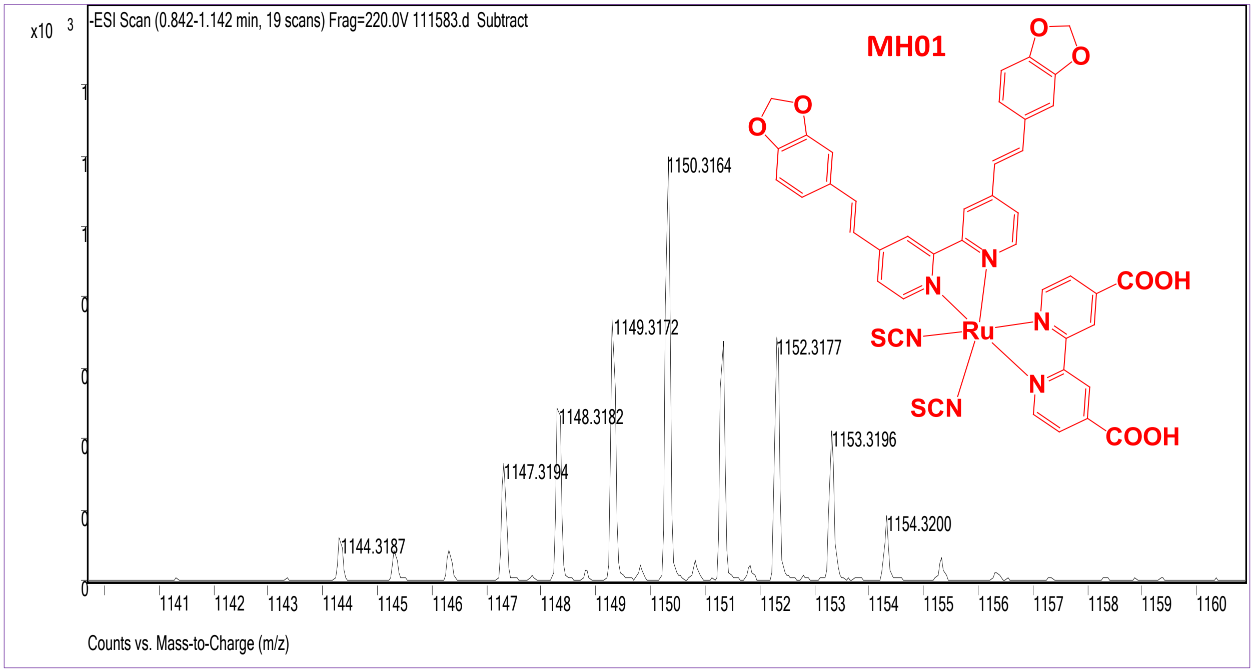

Figure 4S ESI mass spectrum of MH01, Mass 910.0454; $[M - 2H + TBA]^{-1}$; Theo. M/Z = 1150.3145, Found. M/Z 1150.3164, Error = 1.651 ppm.

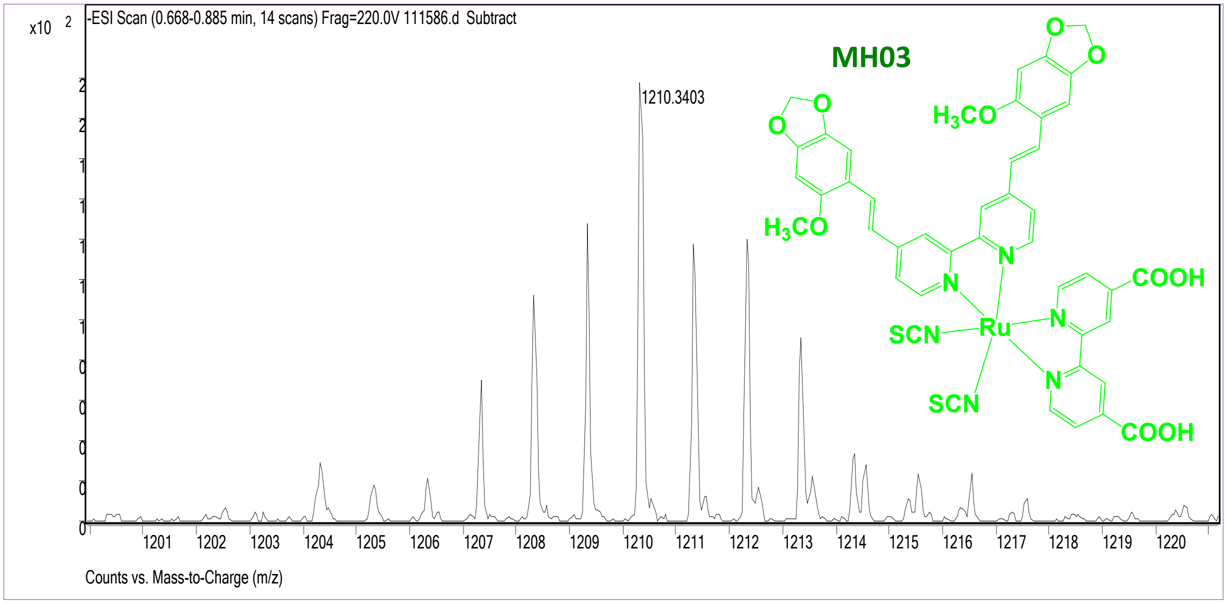

Figure 5S ESI mass spectrum of MH03, Mass 970.0665, [M – 2H + TBA] $^{-1}$, Theo. M/Z = 1210.3356, Found M/Z = 1210.3403, Error = 3.883 ppm.

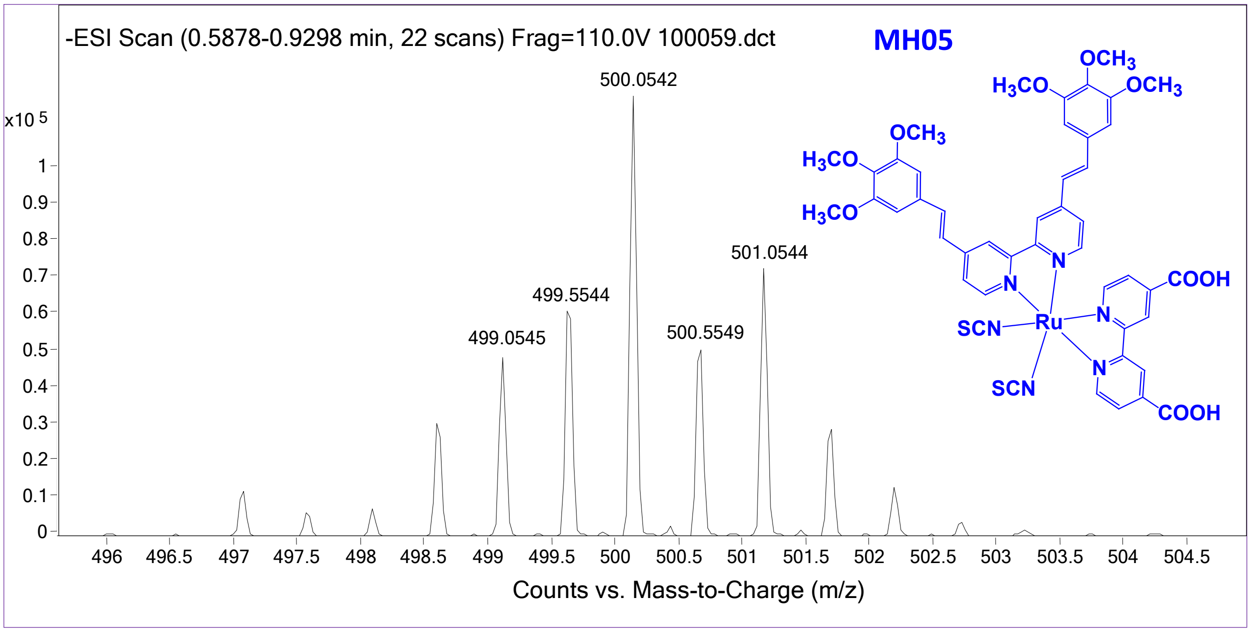

Figure 6S ESI mass spectrum of MH05; Mass 1002.1291 [M - 2H] $^{-2}$; Theo. m/2 = 500.0567, Found m/2 = 500.0542, Error = -5.02 ppm.

1.1.5. ^{1}H-NMR Experiments

^{1}H-NMR experiments were recorded on a Bruker 500 MHz spectrometer at 40 °C using deuterated DMSO-d6 as a solvent unless otherwise specified. Splitting patterns reported here are: s (singlet), d (doublet), dd, (double-of-doublet), t (triplet), p (pentet), and m (multiplet). Chemical shifts (δ) and coupling constants (J) are reported in ppm and Hertz (Hz), respectively. The aliphatic range 0-5ppm is not shown for brevity, unless needed. Figures 7S-9S show the ^{1}H-NMR for the ancillary ligands AL01, AL03, and AL05, respectively, Figures 10Sa-c show the ^{1}H-NMR (recorded on a Bruker 600MHz) of MH01-TBA, and Figures 11S-13S show the ^{1}H-NMR of MH01, MH03, and MH05, respectively.

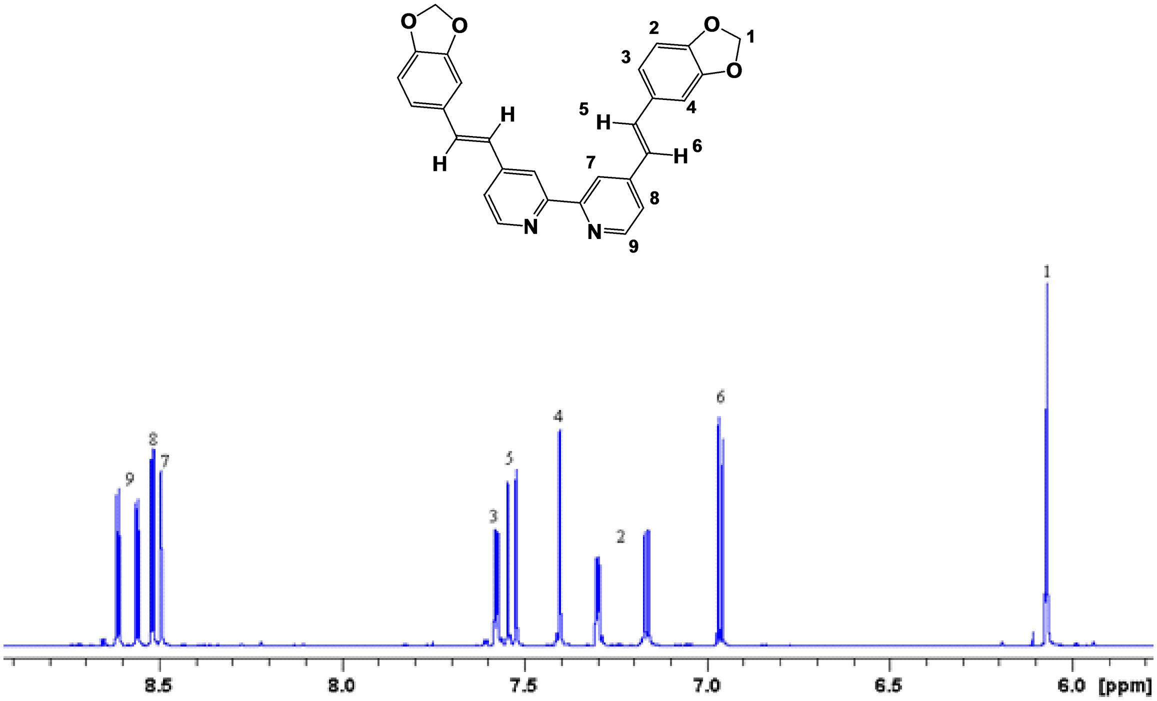

Figure 7S ^{1}H-NMR of the ancillary ligand of MH01 (AL01).

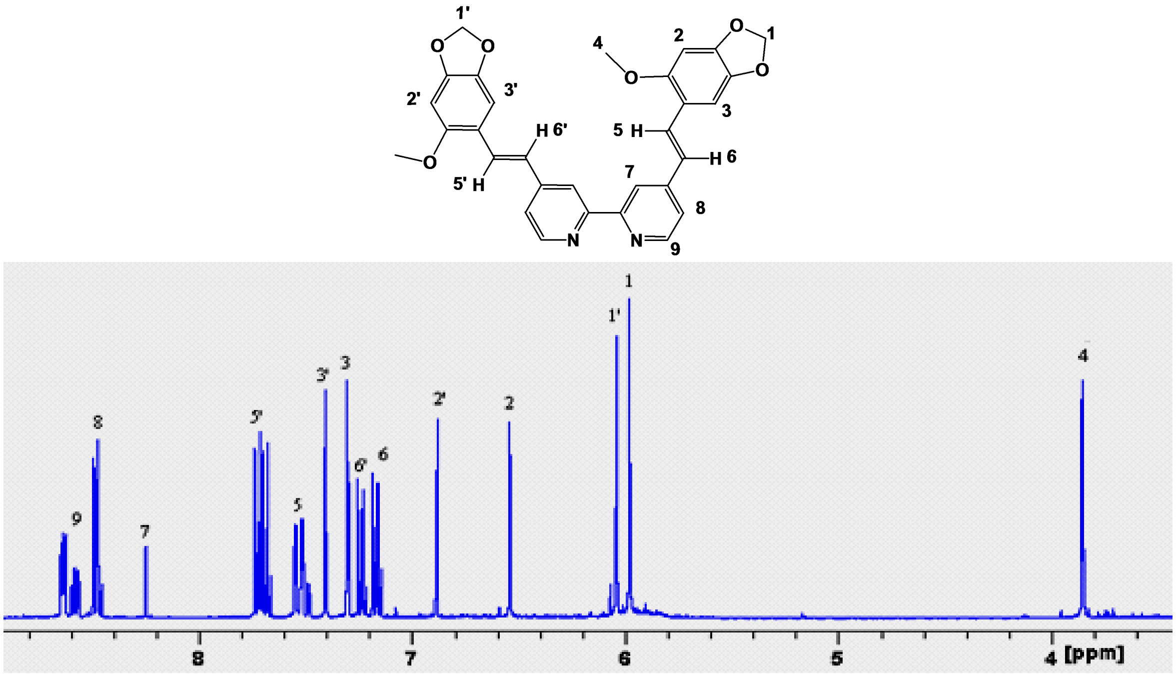

Figure 8S ^{1}H-NMR of ancillary ligand of MH03 (AL03).

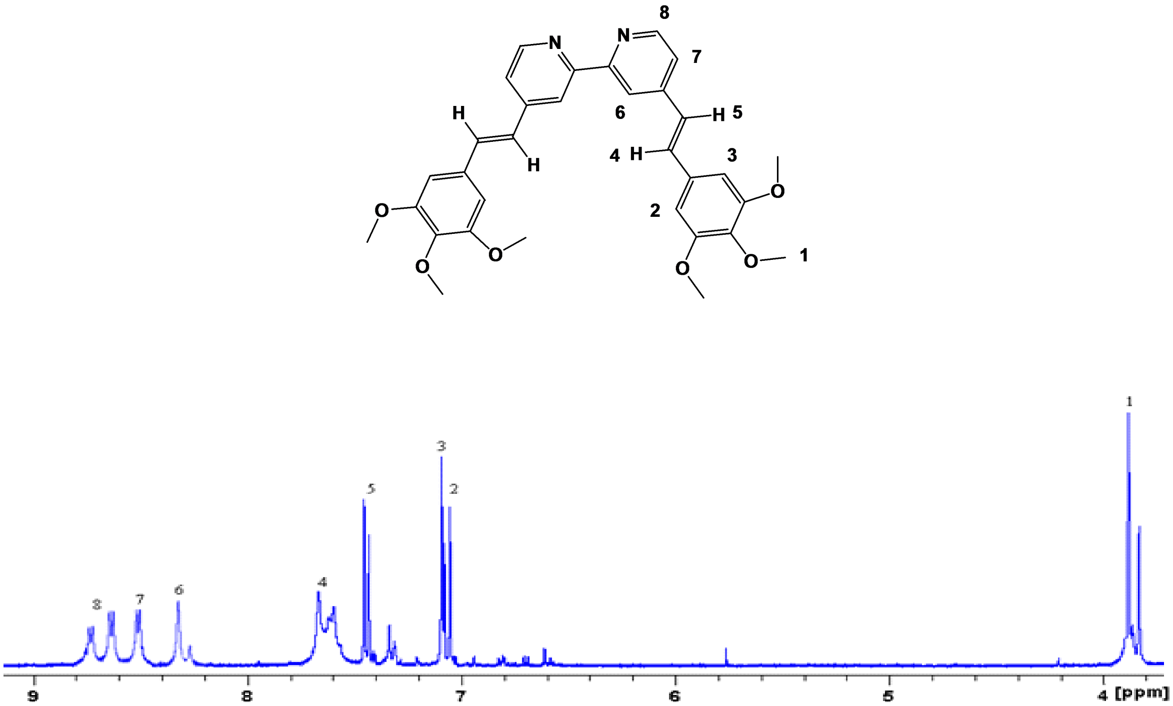

Figure 9S ^{1}H-NMR of ancillary ligand of MH05 (AL05).

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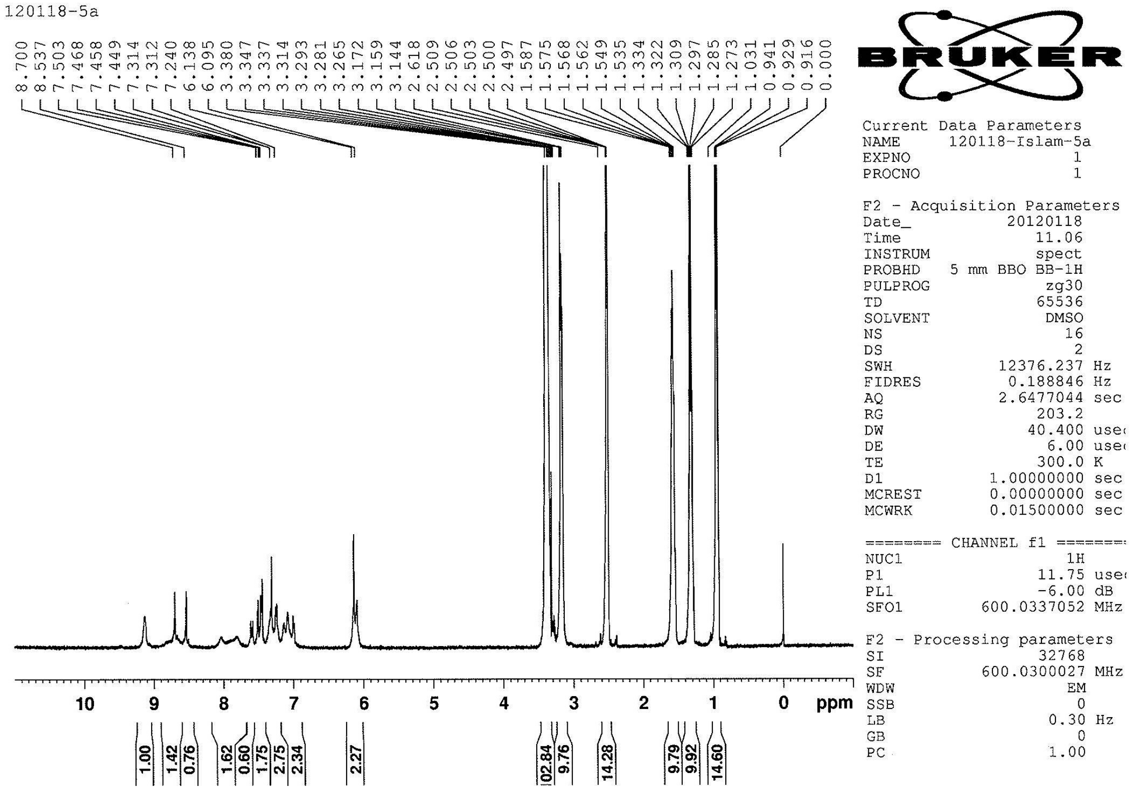

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PROCNO                  1

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TD                  65536
SOLVENT              DMSO
NS                     16
DS                      2
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FIDRES           0.188846 Hz
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RG                  203.2
DW                 40.400 use
DE                   6.00 use
TE                  300.0 K
D1             1.00000000 sec
MCREST         0.00000000 sec
MCWRK          0.01500000 sec

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F2 - Processing parameters
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GB                      0
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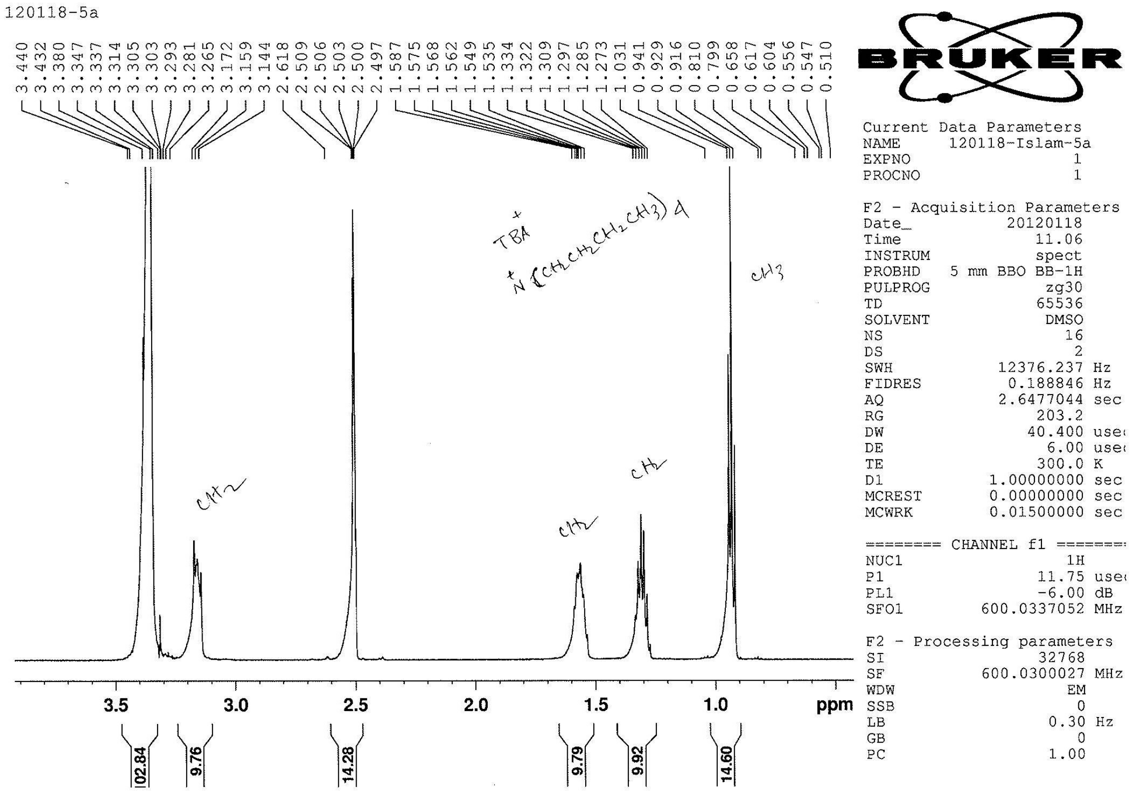
Figure 10Sa ^{1}H-NMR of MH01-TBA.



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DS                    2
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FIDRES         0.188846 Hz
AQ            2.6477044 sec
RG                203.2
DW               40.400 use
DE                 6.00 use
TE                300.0 K
D1           1.00000000 sec
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PL1               -6.00 dB
SFO1        600.0337052 MHz

F2 - Processing parameters
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SF          600.0300027 MHz
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Figure 10Sb Zoom-in on the aliphatic region of MH01-TBA.

^{1}**H-NMR, MH01** (500 MHz, DMSO, 40 °C): δ/ppm 6.3 (S, 4H, CH_2), 7.10 (d, 2H, *J* = 11.0 Hz and 7.02 (d, 2H, *J* = 11.41 Hz, CH=CH), 7.29 (d, 2H, *J* = 7.3 Hz, ArH), 7.57 (s, 2H. ArH), 7.59 (d, 2H, *J* =7.1 Hz, ArH), 7.60 (s, 2H. ArH), 7.82 (d, 2H, *J* = 8.20 Hz, ArH), 8.88 (s, 2H, ArH), 9.04 (s, 2H, ArH), 9.08 (d, 2H, *J* = 8.1 Hz, ArH), 9.39 (d, 2H, *J* = 7.9 Hz ArH).

^{1}**H-NMR, MH03** (500 MHz, DMSO, 40 °C): δ/ppm 3.92 (S, 6H, CH_3), 6.01 (S, 4H, CH_2), 6.53 (d, 2H, *J* = 9.8.0 Hz and 6.61 (d, 2H, *J* = 11.2 Hz, CH=CH), 7.86 (d, 2H, *J* = 7.9 Hz, ArH), 7.95 (s, 2H. ArH), 8.29 (d, 2H, *J* = 8.5 Hz, ArH), 8.9 (s, 2H, ArH), 9.06 (s, 2H, ArH), 8.29 (d, 2H, *J* = 8.5 Hz, ArH), 9.06 (s, 2H, ArH), 9.1 (d, 2H, *J* = 8.6 Hz ArH).

^{1}H-NMR, MH05 (500 MHz, DMSO, 40 °C): δ/ppm 3.88 &3.92 (s, 18H, -OCH_3) 6.17 (s, 2H, ArH), 6.26 (s, 2H, ArH), 6.92 (d, 2H, *J* = 5.5 Hz, and 7.35 (d, 2H *J* = 16.59 Hz CH=CH), 7.50-7.80 (m, 4H, ArH), 8.89 (s, 2H, ArH), 9.12 (s, 2H, ArH), 9.16 (d, 2H, *J* = 5.9 Hz, ArH), 9.46 (d, 2H, *J* = 5.7 Hz, ArH) 14.14 (s, 2H, v. weak, -COOH).

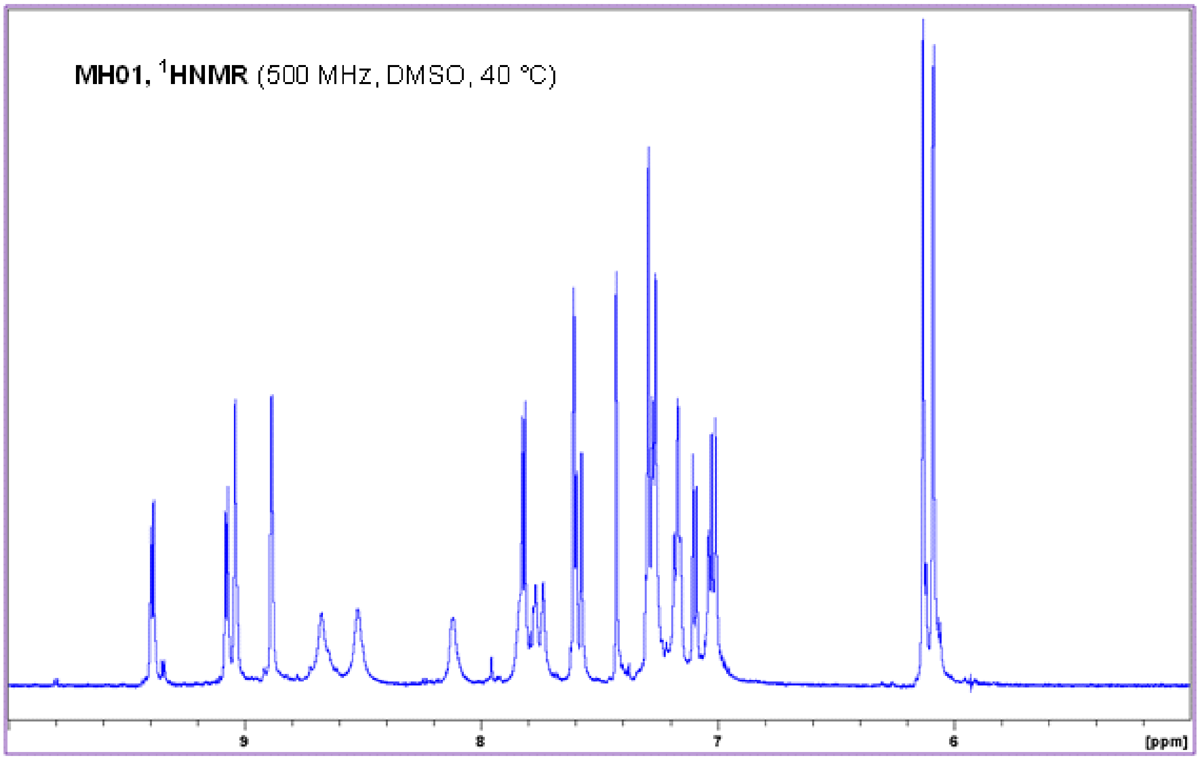

Figure 11S ^{1}H-NMR of MH01.

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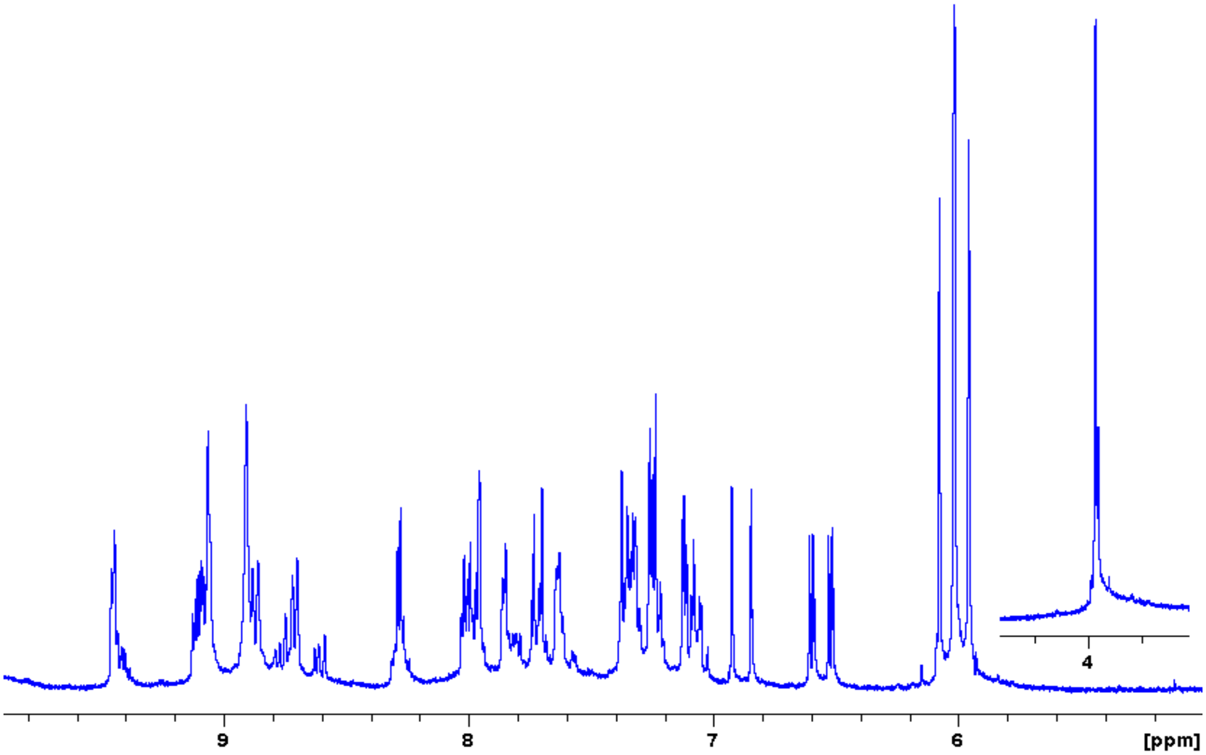

Figure 12S ^{1}H-NMR of MH03**.**

Supporting Information and Experimental Section

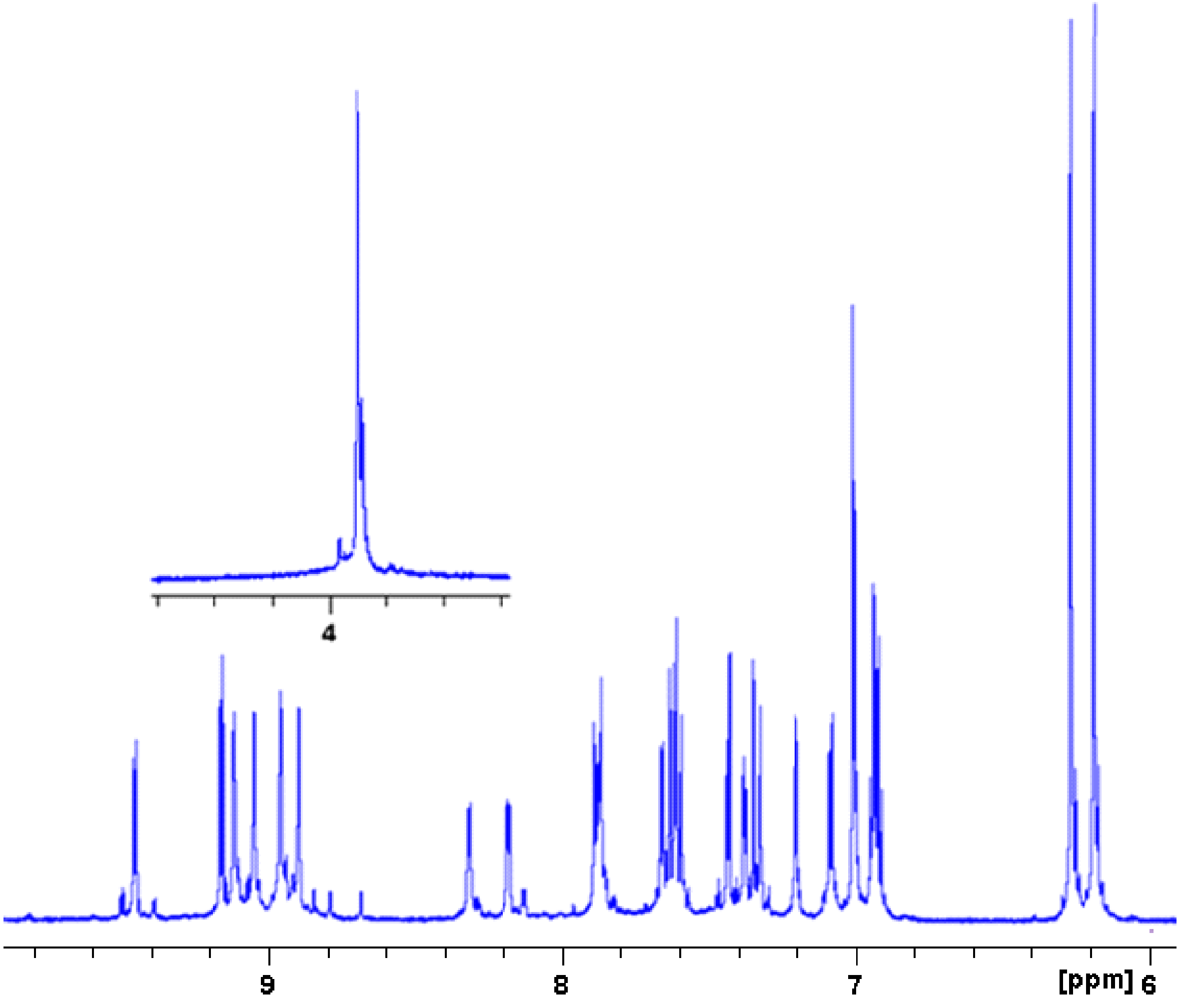

Figure 13S ^{1}H-NMR of MH05.

1.1.6. Elemental Analysis

MH01, Chemical Formula: $C_{42}H_{28}N_6O_8RuS_2$, Calcd. C, 55.44; H, 3.10; N, 9.24. Found: C, 55.21; H, 3.15; N, 9.13.
MH03, Chemical Formula: $C_{44}H_{32}N_6O_{10}RuS_2$, Calcd. C, 54.48; H, 3.33; N, 8.66. Found: C, 54.27; H, 3.41; N, 8.55.
MH05, Chemical Formula: $C_{46}H_{40}N_6O_{10}RuS_2$, Calcd. C, 55.14; H, 4.02; N, 8.39. Found: C, 55.01; H, 4.11; N, 8.26.

1.2.6. TiO_2 Electrode Preparation

A double-layer TiO_2 photoelectrode (10+5) µm in thickness with a 10 µm thick nanoporous layer and a 5 µm thick scattering layer (area: 0.25 cm^2) 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^{-2} and an optical transmission of greater than 80% in the visible range were screen printed using anatase TiO_2 colloids (particle size ~13nm) obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). Nanocrystalline TiO_2 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^{-4} 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_2 surface.

1.2.7. Fabrication of Dye-Sensitized Solar Cell.

Dye-Sensitized Solar Cell were prepared using TiO_2 coated working electrodes and platinum coated counter electrodes, and were sealed using a 40 µm Syrlyn spacer through heating of the polymer frame. The redox electrolyte consisted of a solution of 0.6 M DMPII, 0.05 M I_2, 0.1 M LiI and 0.3-0.5 M TBP in acetonitrile.

1.2.8. Photoelectrochemical Measurements

2.2.8.1. Photovoltaic measurements

Photovoltaic measurements of sealed cells (0.23cm^2 active area) 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 illumination (light intensity: 100 mWcm^{-2}).

1.2.8.2. 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^{-2}) under monochromatic irradiation, q is the elementary charge, λ is the wavelength of incident radiation in nm and P_0 is the incident radiative flux in Wm^{-2} [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.

1.2.8.3. Photoemission Yield Spectrometer (AC3) and E_{0-0} Measurements

The experimental HOMO and E_{0-0} energy values for MH01, MH02, MH05 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 10S-13S show the HOMO energies of MH01, MH03, MH-05 and N719, respectively.

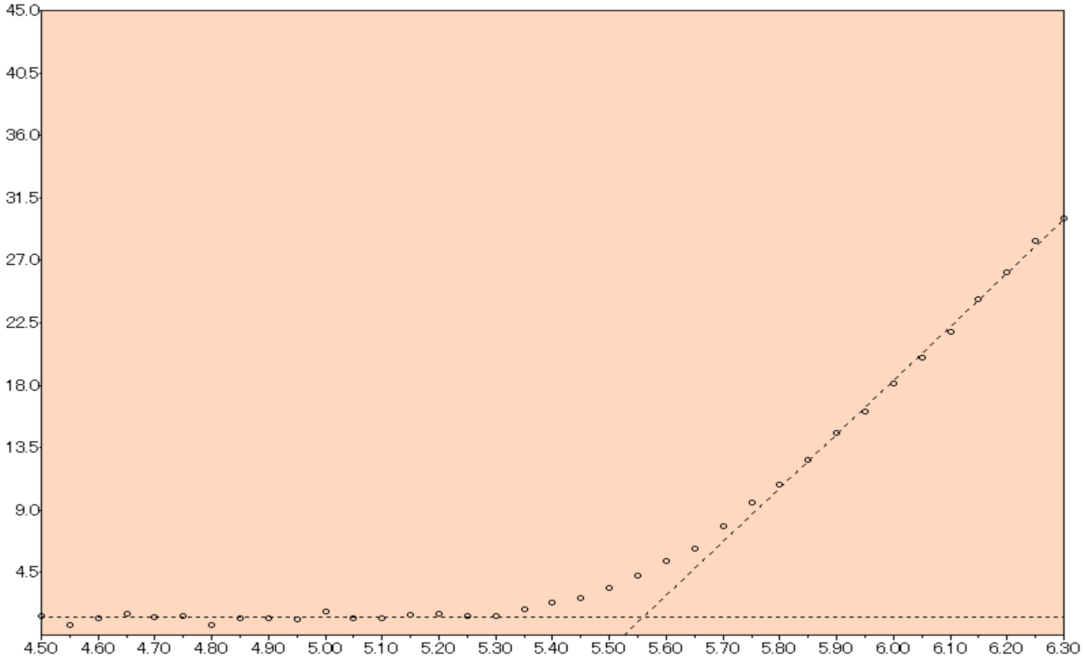

Figure 10S HOMO energy (-5.52eV) of MH01**.**

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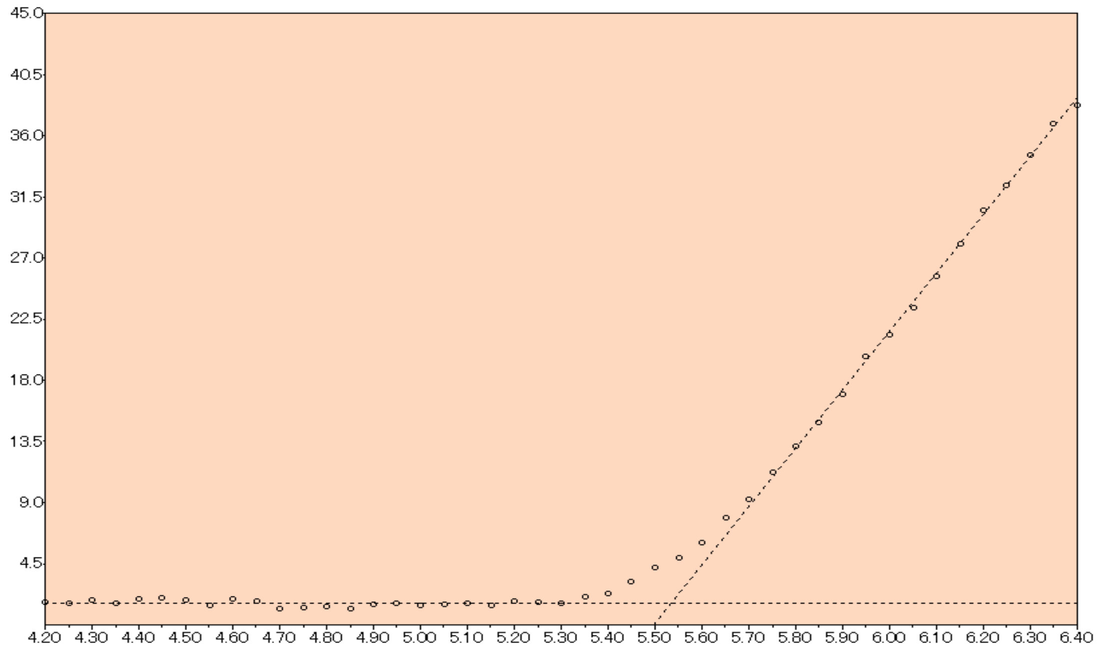

Figure 11S HOMO energy (-5.50eV) of MH03**.**

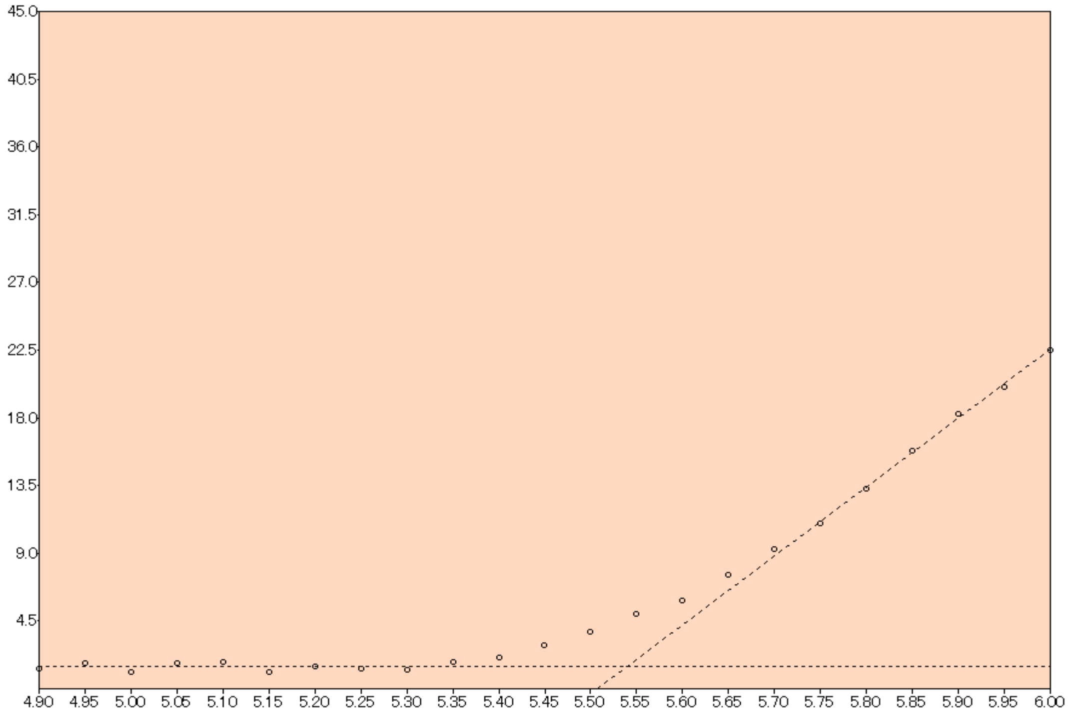

Figure 12S HOMO energy (-5.51eV) of MH05**.**

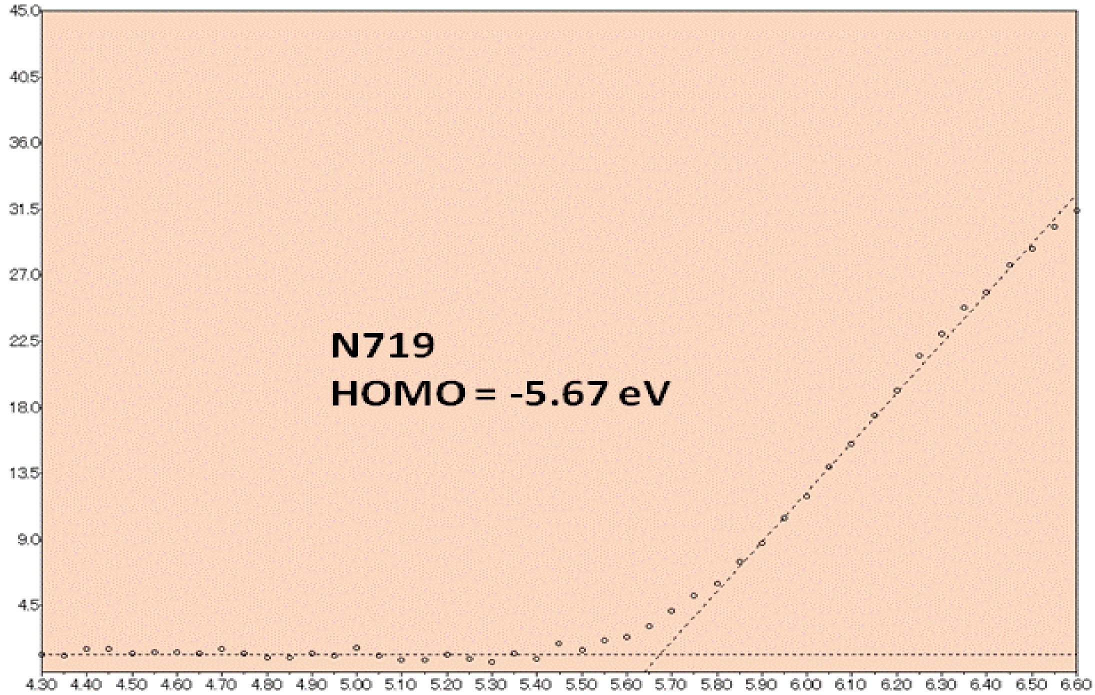

Figure 13S HOMO energy (**-5.67eV**) of N719.

1.2.8.4. Electrochemical impedance spectroscopy (EIS) and intensity modulated photovoltage spectroscopy (IMVS) measurements

The IMVS spectra were measured with a potentiostat (Solartron1287) equipped with a frequency response analyzer (Solartron1255B) at an open-circuit condition, based on a monochromatic illumination (420 nm) controlled by Labview system, to obtain the photovoltaic response induced by the modulated light. The modulated light was driven with a 10% AC perturbation current superimposed on a DC current in a frequency range from 0.1 to 10^6 Hz. The charge extraction method (CEM) was performed with the same monochromatic light source. The solar cell was illuminated at an open-circuit condition for 5 s to attain a steady state and then the light source was switched off when the device simultaneously switched to a short-circuit condition to extract the charges generated at that light intensity. The electrochemical impedance spectra were measured with an impedance analyzer (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination using a solar simulator (WXS-155S-10: Wacom Denso Co. Japan). EIS spectra were recorded over a frequency range of 10^2 to 10^6 Hz at 298 K. The applied bias voltage and AC amplitude were set at the *Voc* of the DSCs. The applied bias voltage and AC amplitude were set at the *Voc* of the DSCs. The electrical impedance spectra were characterized using Z-View software (Solartron Analytical).

1.2.9. Synthesis

1.2.9.1 Ligands

1.2.9.1.1 4,4'-Bis-(2-benzo[1,3]dioxol-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, 5.428×10^{-3} mol) and Benzo[1,3]dioxole-5-carbaldehyde (1.712g, 1.085×10^{-2} mol, 5% excess was used to drive the reaction to completion), and three equivalent of $Si(CH_3)_3Cl$. The reaction temperature was raised to 100 ^{o}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 ligands

1.2.9.1.2 4,4'-Bis-[2-(6-methoxy-benzo[1,3]dioxol-5-yl)-vinyl]-[2,2']bipyridinyl

The title ligand was synthesized in 92% yield the procedure described above in 1.2.9.1.1

1.2.9.1.3 4,4'-Bis-[2-(3,4,5-trimethoxy-phenyl)-vinyl]-[2,2']bipyridinyl

The title ligand was synthesized in 90% yield according the procedure described above in 1.2.9.1.1

1.2.9.2 Synthesis of 2, 2’-Bipyridinyl-4, 4’-dicarboxylic acid

2, 2’-Bipyridinyl-4, 4’-dicarboxylic acid was synthesized in 93% yield according to a previously reported procedure [5]

1.2.9.3 Synthesis of complexes MH01, MH01-TBA, MH03 and MH05

1.2.9.3.1 Synthesis of MH01, modified from Graetzel Method.

The synthesis of **MH01** 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 x 10^{-4} mol) and 4,4'-Bis-(2-benzo[1,3]dioxol-5-yl-vinyl)-[2,2']bipyridinyl (0.435 g, 9.797 x 10^{-4} mol). The reaction mixture was stirred at 90 °C for 4h. Then, 2,2'-bipyridyl-4,4'-dicarboxalic acid was added (0.239 g, 9.797 x 10^{-4} mol) and the temperature was raised to 130°C and allowed to run for 6 hours. After the 6 hours, excess of NH_4NCS (0.5g) was added to the reaction mixture, and the reaction mixture was allowed to run for another 4h at 130°C. The last two steps of the reaction were monitored for completion by taking aliquots from the reaction mixture every 60 minutes and measuring its absorption spectrum until there was no increase in the absorbance of the MLCT peaks with respect to the π-π^* peak. 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 94% yield, with respect to the starting material.

Synthesis of MH01-TBA

MH01-TBA was synthesized by adding MH01 (0.1g) to 20 mL of H_2O/MeOH (11:9) and tetrabutylammonium hydroxide (0.0285g), and the pH of the solution was kept at 9. To this solution, 0.1g of tetrabutylammonium thiocyanate was added. The resulting solution was filtered to remove any insoluble material, and the pH was adjusted to 4.0 using dilute HCl. A dense precipitate formed immediately and the suspension was concentrated to 10 mL. The solution was filtered using a sintered glass crucible, and the precipitate was dried under vacuum to yield tetrabutylammonium salt, MH01-TBA, which was confirmed using ^{1}H-NMR.

Complexes MH01, MH03, and MH05 were synthesized according the above procedure in 93%, 95%, 95% and 91% yield, respectively. Scheme 1 summarizes the general synthetic route for complexes MH01, MH03 and MH05.

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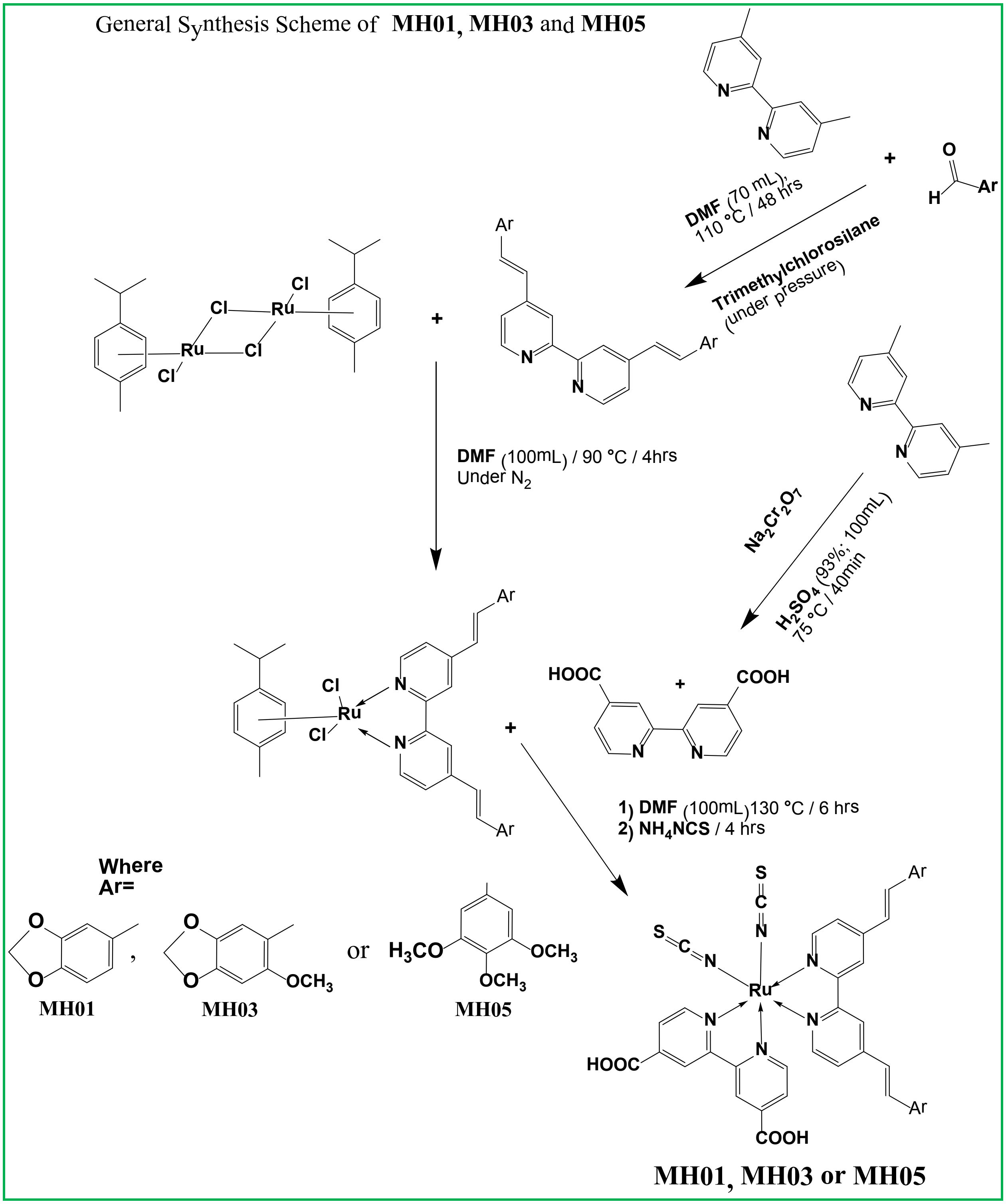

Scheme 1 General route for the synthesis of complexes MH01, MH03 and MH05.

1.2.10 Purification

MH01 was purified on a column using Sephadex LH-20 as the stationary phase and pure methanol as the mobile phase. The crude dye of MH01 was dissolved in a mixture of methanol and TBAOH 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 2.0, and the acidified solution was kept in a refrigerator for 48 hours. Then, the precipitate was filtered, washed with plenty of de-ionized water to remove remaining HCl. The same purification procedure was repeated three times in order to obtain MH01 in the pure form. Complexes MH03 and MH05 was purified using the above procedure.

1.2.11 Molecular Modeling

Equilibrium molecular geometries of MH01, MH03, and MH05 were calculated using the energy functional 3-Parameter (Exchange), Lee, Yang and Parr (B3LYP) [6,7] and the full-electron basis set Density Gauss double-zeta with polarization functions (DGDZVP) [8,9]. The geometry optimization calculations were followed by energy calculations using TD-DFT utilizing the energy functional B3LYP and the basis set DGDZVP. The solvent (DMF) effect was accounted for by using the polarizable continuum model (PCM), implemented in Gaussian 09, and the ground and excited states oxidation potentials were calculated. All DFT and TD-DFT jobs were submitted remotely at East Carolina University's Supercomputer Jasta.

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