Structure-property relationship of extended π -conjugation of ancillary ligands with and without electron donor of heteroleptic Ru (II) bipyridyl complexes for high efficiency dye-sensitized solar cells

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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. The aldehydes were purchased from Sigma-Aldrich with 99% purity. 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, show the FT-IR of **MH06 and MH11** in the pure form, respectively.



Figure 1S ATR/FT-IR of MH06.



Figure 2S ATR/FT-IR of MH11.

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 20 scans in the case of **MH06**, 40 scans in the case of **MH11** were averaged. Figures 3S-4S show the ESI-MS of **MH06** and **MH11** with one TBA per molecule, singly charged, with identical pattern of ruthenium isotopes.



Figure 3S ESI mass spectrum of **MH06**, Mass 982.1181; $[M - 2H + TBA]^{-1}$; Theo. M/Z = 1222.3873, Found. M/Z 1222.3926, Error = 4.335 ppm.



Figure 4S ESI mass spectrum of **MH11**, Mass 910.0453, $[M - 2H + TBA]^{-1}$, Theo. M/Z = 1310.3974, Found M/Z = 1310.4038, Error = -4.884 ppm.

1.2.5. ¹H-NMR Experiments

¹H-NMR experiments were recorded on a Bruker 500 MHz spectrometer at 40 °C using deuterated DMSO-d6 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 (δ) and coupling constants (J) are reported in ppm and Hertz (Hz), respectively. The aliphatic range 0-5ppm is not shown for brevity. Figures 5S-6S show the H-NMR for **MH06** and **MH11**, respectively.



Figure 5S ¹H-NMR of MH06.



Figure 6S ¹H-NMR of **MH11**.

1.2.6. TiO₂ Electrode Preparation

A double-layer TiO₂ photoelectrode (10+5) µm in thickness with a 10 µm thick nanoporous layer and a 5 µm thick scattering layer (area: 0.25 cm²) 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 TiO₂ colloids (particle size ~13nm) obtained from commercial sources (Ti-Nanoxide D/SP, Solaronix). Nanocrystalline TiO₂ 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.

Photovoltaic and IPCE measurements were made on sandwich cells, which were prepared using TiO_2 coated working electrodes and platinum coated counter electrodes, and were sealed using a 40 μ m Syrlyn spacer through heating of the polymer frame. The redox electrolyte consisted of a solution of 0.6 M DMPII, 0.05 M I₂, 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 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^{-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].

$$IPCE(\lambda) = 1240 \left(\frac{I_{SC}}{q\lambda P_0}\right)$$
 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 E₀₋₀ Measurements

The experimental HOMO and $E_{0.0}$ energy values for **MH06** and **MH11** 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 7S-9S show the HOMO energies of **MH06**, **MH11** and **N719**, respectively.



Figure 7S HOMO energy (-5.51eV) of MH06.



Figure 8S HOMO energy (-5.49eV) of MH11.

1.2.8.4. Photoluminescence emission decay

Emission decay spectra were recorded in DMF solutions while maintaining the optical absobtivity at 0.1 Abs, using a Fluorolog-311 at room temperature. The emission decays were recorded upon exciting at 454 nm using time-correlated single photon counting (TCSPC) procedure, after measurement the decay the data was further fitted using fitting model 2 (two-exponential) at a channel range of channel range 1000nm-3000nm.



Figure 9S Time-Correlated Single Photon Counting (TCSPC), Emission Decay (6.25 ns)



Figure 10S Time-Correlated Single Photon Counting (TCSPC), Emission Decay (6.47 ns)

1.2.9. Synthesis of Ligands

1.2.9.1. 4,4'-Bis-[2-(4-methoxy-naphthalen-1-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 x 10^{-3} mol) and 4-Methoxy-naphthalene-1-carbaldehyde (2.0203g, 1.085 x 10^{-2} mol, 5% excess was used to drive the reaction to completion), and three equivalent of Si(CH₃)₃Cl. 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 94% yield, which was used for the next step after washing with toluene. The other 4, 4'-Bis-(2-pyren-1-yl-vinyl)-[2, 2']bipyridinyl ligand was prepared using same procedure with a 96% yield.

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 MH06 and MH11

The synthesis of MH06 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-(4-methoxy-naphthalen-1-yl)-vinyl]-[2,2']bipyridinyl (0.5100g, 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 NH₄NCS (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 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 97% yield, with respect to the starting material. Complexes **MH11** were prepared using same procedure in 94% crude yield. Scheme 1 summarizes the general synthetic route for complexes **MH06** and **MH 11**.

Scheme 1 General route for the synthesis of complexes MH06 and MH11.

1.2.10 Purification

MH06 was purified on a column using Sephadex LH-20 as the stationary phase and pure methanol as the mobile phase. The crude dye of **MH06** 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 3.0, and the acidified solution was kept in a refrigerator for 12 hours. Then, the precipitate was filtered, washed with plenty of deionized water to remove remaining HCl. The same purification procedure was repeated three times in order to obtain **MH11** in the pure form.

1.2.11. Molecular Modeling

Equilibrium molecular geometries of **MH08-10** and **N719** were calculated using the energy functional 3-Parameter (Exchange), Lee, Yang and Parr (B3LYP) [5,6] and the full-electron basis set Density Gauss double-zeta with polarization functions (DGDZVP) [7,8]. 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 account 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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