

# Influence of Mono Versus Bis-Electron-Donor Ancillary Ligands in Heteroleptic Ru (II) Bipyridyl Complexes on the Electron Injection from the First Excited Singlet and Triplet States in Dye-sensitized Solar Cells

Hammad Cheema<sup>a</sup>, Ashraful Islam<sup>b</sup>, Liyuan Han<sup>b</sup>, Bhoj Gautam<sup>c</sup> Robert Younts<sup>c</sup>,

Kenan Gundogdu<sup>c</sup>, Ahmed El-Shafei<sup>a\*</sup>

<sup>a</sup>Polymer and Color Chemistry Program, North Carolina State University, Raleigh, NC, 27695, USA

<sup>b</sup>Photovoltaic Materials Unit, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan.

<sup>c</sup>Physics Department, North Carolina State University, Raleigh, NC, 27695, USA

\*Corresponding author: [Ahmed\\_El-Shafei@ncsu.edu](mailto:Ahmed_El-Shafei@ncsu.edu)

## **Materials and Equipment**

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

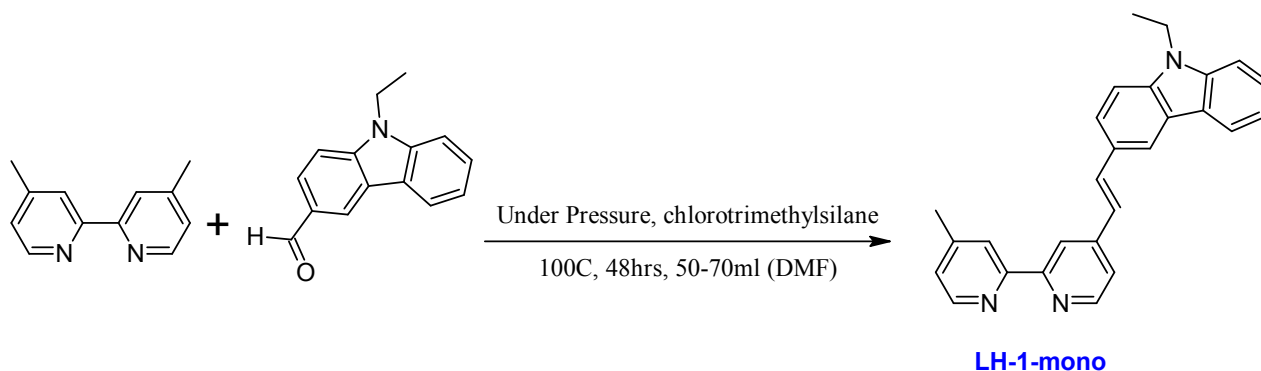
The mass spectra were obtained using electrospray ionization mass spectrometry (ESI-MS) on an Agilent Technologies (Santa Clara, California) 6210 LC-TOF mass spectrometer by dissolving samples in methanol containing 1% TBAOH. FT-IR (ATR) spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer (Thermo Scientific, USA) and UV-Visible spectra were measured by using Cary 300 spectrophotometer. Fluorescence and emission decay were recorded at room temperature on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon Inc.). <sup>1</sup>H-NMR spectra were recorded in a Bruker 500 MHz spectrometer.

### **1. Synthesis of ligands**

#### **1.1. Synthesis of 4-methyl,4'-(E)-(9-ethyl-9H-carbazol-3-yl)vinyl)-2,2'-bipyridine (LH-1-mono)**

Synthetic route for the synthesis of LH-1-mono is given in Scheme1. The antenna ligand 4-methyl,4'-(E)-(9-ethyl-9H-carbazol-3-yl)vinyl)-2,2'-bipyridine was synthesized under pressure in a glass tube containing 4,4'-dimethyl-2,2'-bipyridine (1g, 5mmol), 9-ethyl-9H-carbazole-3-carbaldehyde (1.116g, 5mmol), 17.5mmol of chlorotrimethylsilane, and a magnetic stirrer bar in 70ml of anhydrous DMF <sup>1,2</sup>. Once the tube was closed with the cap the reaction temperature was raised to 100°C and allowed to run for 48 hours with continuous stirring. During the course of the 48hours, the color of the reaction mixture changed to orange. At the end of the reaction, the pressure was released after cooling the tube and the solvent was removed using rotary

evaporator, and the dark orange product was precipitated by the addition of water. Finally vacuum filtration was performed to furnish the antenna ligand which was thoroughly washed with water and toluene in sequence to obtain LH-1-mono. It was then dried for overnight at 50 °C to obtain 65% yield. LH-1-mono was used for next step without further purification.



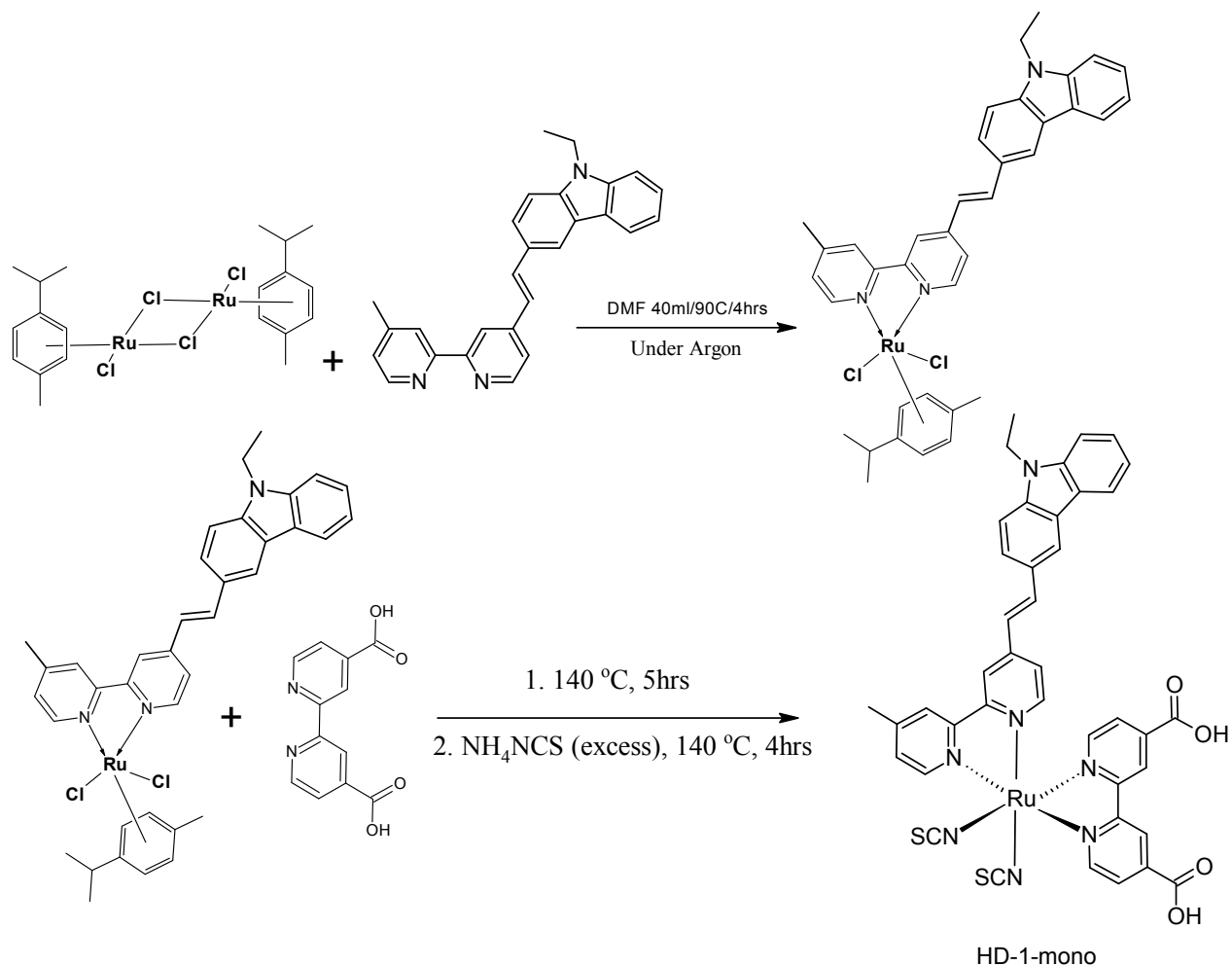
**Scheme 1.** Synthesis of Ligands LH-1-mono

### 1.2. Synthesis of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid

The 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid was synthesized according to published procedure<sup>3</sup>. In a three neck round bottom flask 4,4'-Dimethyl-2,2'-bipyridine (3 g, 16.3 mmol) was gradually added to a stirred solution of sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7$ ) (10.9g, 36.5 mmol) in concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (93%, 45 ml) and stirred for 30 min at 75°C. After 30 min, the dark green reaction mixture was poured into cold water forming a light yellow precipitate. The precipitate was then filtered under vacuum and dissolved in 10 % aq. Sodium hydroxide. The product was crystallized by slowly acidifying the solution with 10 % aq. hydrochloric acid at a pH of 2. The precipitation and acidification process was repeated three times to obtain the white chromium free precipitates of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid (2.56g, 90%).

### 1.3 Synthesis of HD-1-mono

Chemical route for the synthesis of HD-1-mono is shown in Scheme 2. The synthesis was carried out in a one-pot three-step reaction in a 250 ml reaction flask equipped with a condenser and magnetic stirrer bar under Argon. The flask was charged with anhydrous DMF, dichloro-(p-cymene)-Ruthenium (II) dimer (0.16g, 0.25mmol) and LH-1-mono (0.2g, 0.5mmol). The reaction mixture was stirred at 90 °C for 4h. Then, 2,2'-bipyridyl-4,4'-dicarboxylic acid was added (0.12g, 0.5mmol) and the temperature was raised to 140°C and allowed to run for 5 hours. After the 5 hours, excess of NH<sub>4</sub>NCS (0.3g) was added to the reaction mixture, and the reaction mixture was allowed to run for another 4h at 140°C. The reaction mixture was cooled down to room temperature and DMF was removed using a rotary evaporator. Ice was added to the flask and the insoluble solid was vacuum filtered and washed with de-ionized water and diethyl ether. The black color solid product was dried overnight and 0.295g of crude product was collected. After drying, HD-1-mono was dissolved in methanol with the addition of Tetrabutylammonium hydroxide (TBAOH). HD-1-mono was run through the column containing Sephadex LH-20 for three times. The main band was collected and acidified using 0.1M HCl to reduce the pH to 2.0 and allowed to precipitate for 48 hours at low temperature, precipitate was filtered, washed with plenty of de-ionized water to bring pH to neutral. The pure dye was then dried overnight and collected (0.120g, 50-57%).



**Scheme 2.** Synthetic route for HD-1-mono

## 2. Analytical Measurements

### 2.1. UV-Visible spectra

UV-Visible spectra of HD-1-mono, NCSU-10 and N719 were measured using a concentration of  $2.0 \times 10^{-5}$  mole in DMF (Anhydrous). The spectra were recorded at room temperature in a quartz cell (1.0 cm) on a Cary 3 Spectrophotometer.

### 2.2. Emission and TCSPC Spectroscopy

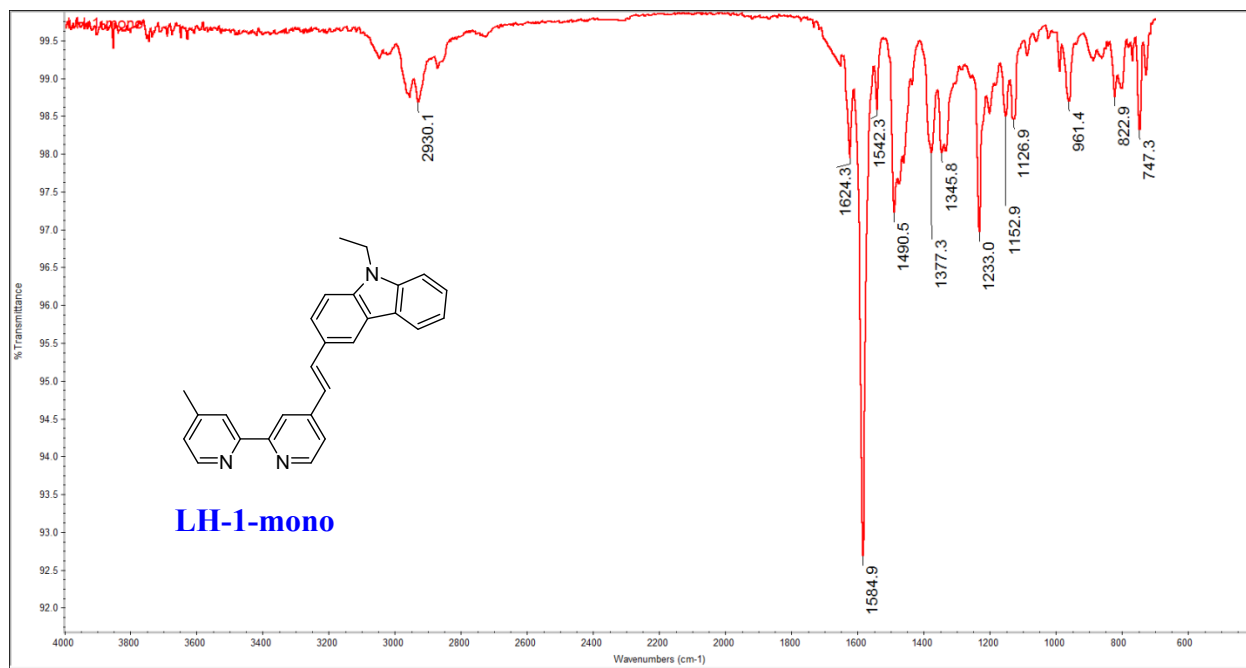
Fluorescence spectra were recorded in a 1 cm path length quartz cell using  $2 \times 10^{-5}$  M solutions on Fluorolog-311. The emitted light was detected in the steady state mode using a Hamamatsu

R2658 detector. The emission was measured in the steady state mode by exciting at the MLCT  $\lambda_{\text{max}}$  for each dye with exit and entrance slits set at 11 nm at an integration time of 0.1sec.

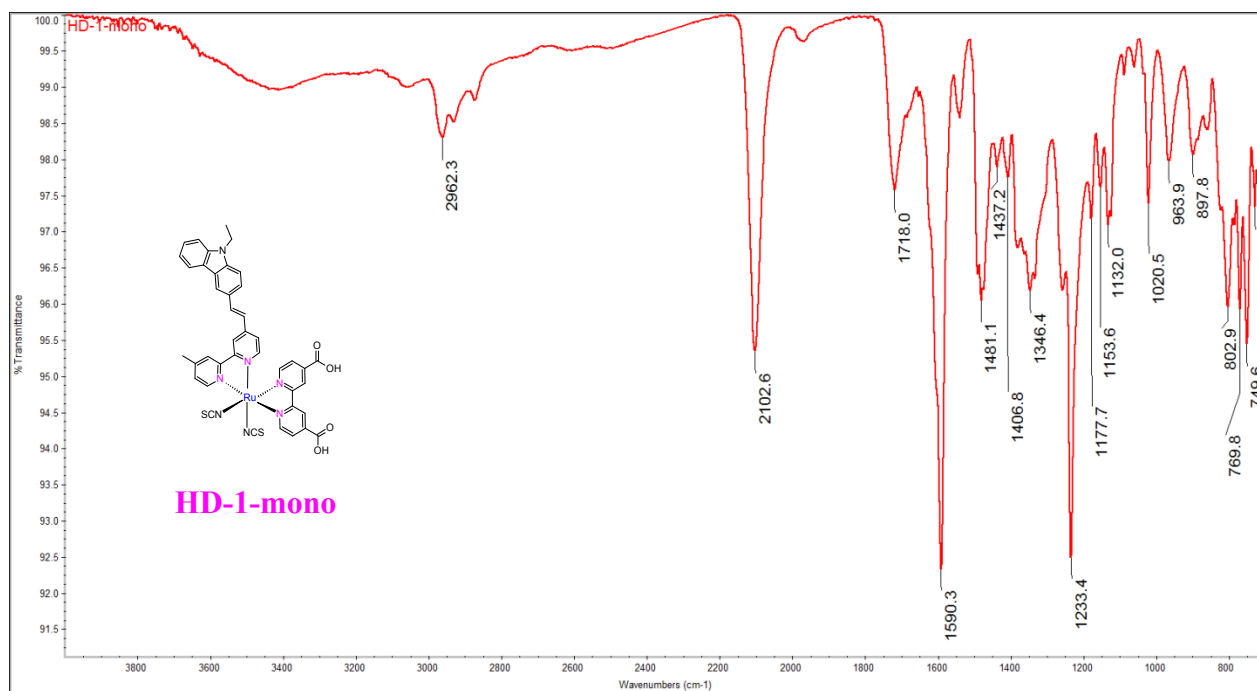
In the case of lifetime measurements, time-correlated photoluminescence spectroscopy was performed on solution of dyes in DMF by exciting the sample using a pulse laser (460nm, NanoLED) at a 1 MHz repetition rate with band pass of 15nm. The time of arrival of the photon counting (TAC) range was adjusted to 200 ns in order to measure the emission decay lifetime (lowest excited state lifetime) using time-correlated single photon counting (TCSPC) mode. The lifetime decay spectra were then fitted with DAS (data analysis software) from Horiba Scientific. TCSPC studies on original cells were carried out using the similar method.

### **2.3. 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, and 2S, show the FT-IR for the ligand LH-1-mono and HD-1-mono in the pure form, respectively.



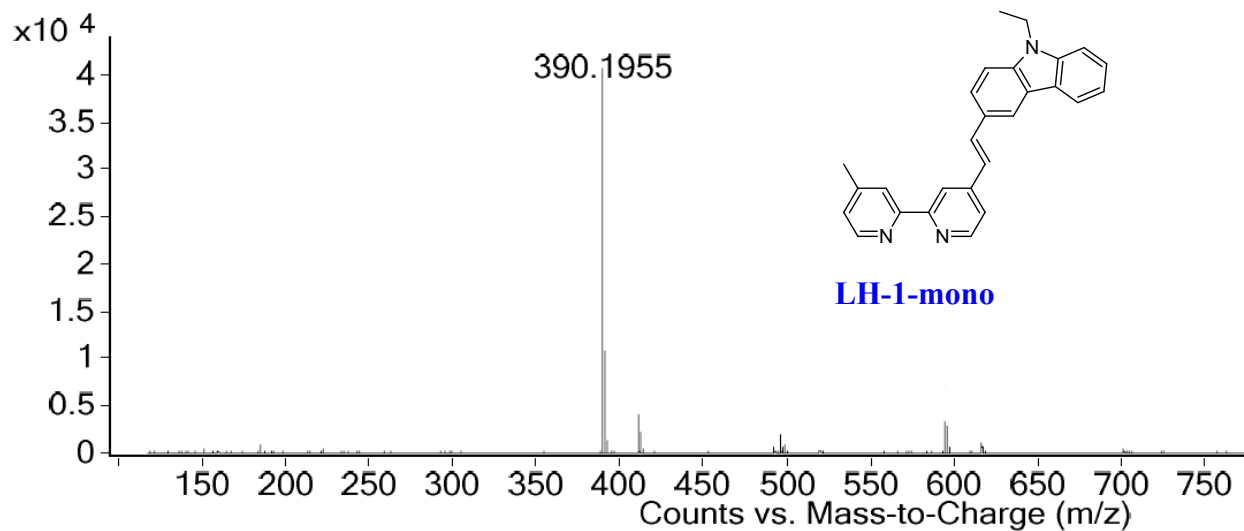
**Figure 1S.** ATR/FT-IR of LH-1-mono



**Figure 2S.** ATR/FT-IR of HD-1-mono

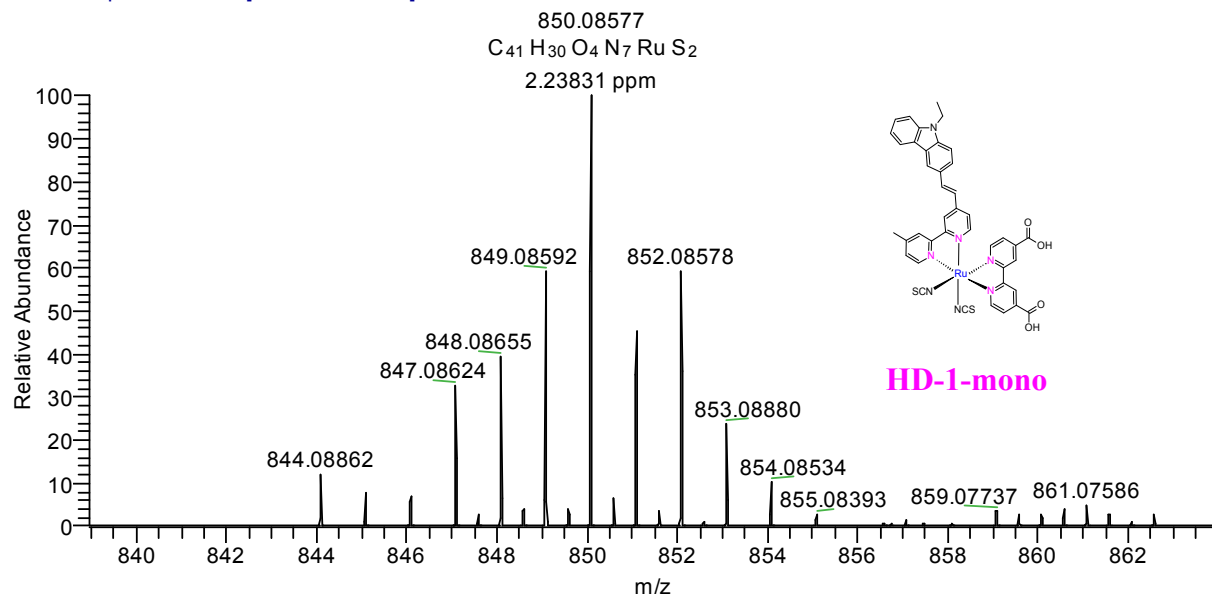
HD-1-mono: 2102.6 cm<sup>-1</sup> (-NCS stretch, N-bonded isomer, very strong); 1718 cm<sup>-1</sup> (C=O stretch of -COOH)

## 2.4. ESI-mass of LH-1-mono and HD-1-mono



**Figure 3S.** ESI mass spectrum of **LH-1-mono**, Mass 389.1892;  $[M + 1H]^+$ ; Theo. M/Z = 390.1965, Found. M/Z, 390.1955, Error = 2.65 ppm

131719\_HD1\_Mono\_NEG#148 RT: 0.66 AV: 1 SB: 8 0.85-0.88 NL: 5.58E5  
T: FTMS - p ESI Full ms [250.00-1200.00]



**Figure 4S.** ESI mass spectrum of **HD-1-mono**, Mass 851.92;  $[M - 1H]^{-1}$ ; Theo. M/Z = 850.08357, Found. M/Z 850.08577, Error = 2.23831 ppm.



## 2.5. <sup>1</sup>H-NMR spectroscopy

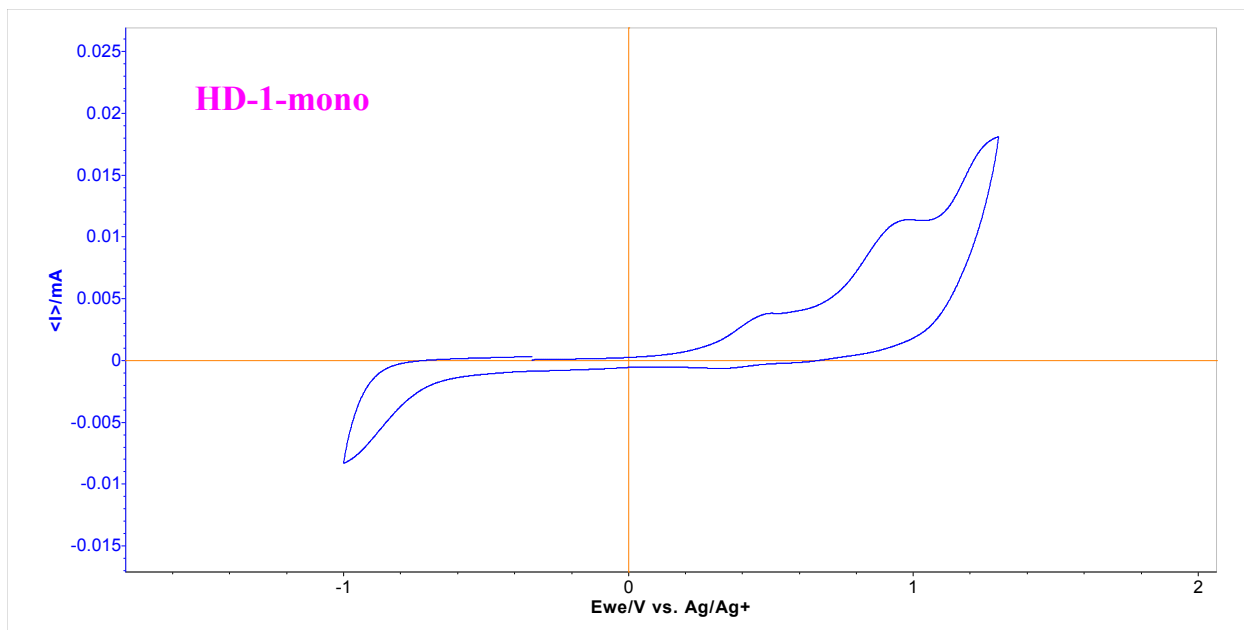
<sup>1</sup>H-NMR spectra were recorded in DMSO at room temperature using a Varian 400 and Bruker 500 MHz spectrometer. Splitting patterns reported here are: s (singlet), d (doublet), dd, (double-of-doublet), t (triplet), p (pentet), and m (multiplet). Chemical shifts ( $\delta$ ) and coupling constants ( $J$ ) are reported in ppm and Hertz (Hz), respectively. TBA (tetrabutyl ammonium) residues were observed in the alkyl part of the <sup>1</sup>H nmr spectrum of HD-1-mono.

**<sup>1</sup>H-NMR, LH-1-mono (400 MHz, DMSO-d<sub>6</sub>):**  $\delta$  8.82 (d,  $J$  = 6.8 Hz, 1H), 8.74 (d,  $J$  = 5.4, 2H), 8.55 (d,  $J$  = 18.9 Hz, 2H), 8.26 – 8.11 (m, 2H), 7.92 (t,  $J$  = 8.4 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.29 (d,  $J$  = 9.3, 2H), 4.51 (q, 2H), 2.57 (s, 3H), 1.36 (t,  $J$  = 5.2 Hz, 3H).

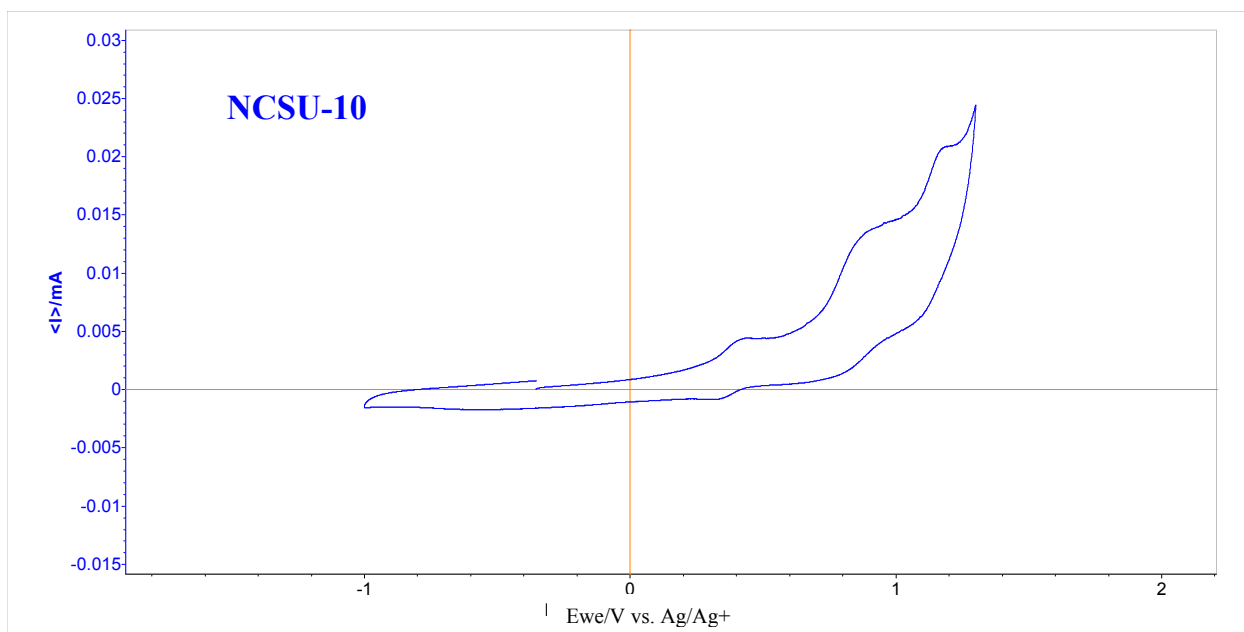
**<sup>1</sup>H-NMR, HD-1-mono (500 MHz, DMSO-d<sub>6</sub>):**  $\delta$  9.44 (s, 1H), 9.17 (s, 1H), 9.07 (d,  $J$  = 18.2 Hz, 2H),  $\delta$  8.82 (d,  $J$  = 6.8 Hz, 1H), 8.74 (d,  $J$  = 5.4, 2H), 8.55 (d,  $J$  = 8.9 Hz, 2H), 8.26 – 8.11 (m, 4H), 7.92 (t,  $J$  = 8.4 Hz, 2H), 7.66 (m, 2H), 7.30 (d,  $J$  = 10.0 Hz, 2H), 4.50 (q, 3H), 2.55 (s, 3H), 1.38 (t, 3H).

## 2.6 CV and Photoemission Yield Spectrometer (AC3)

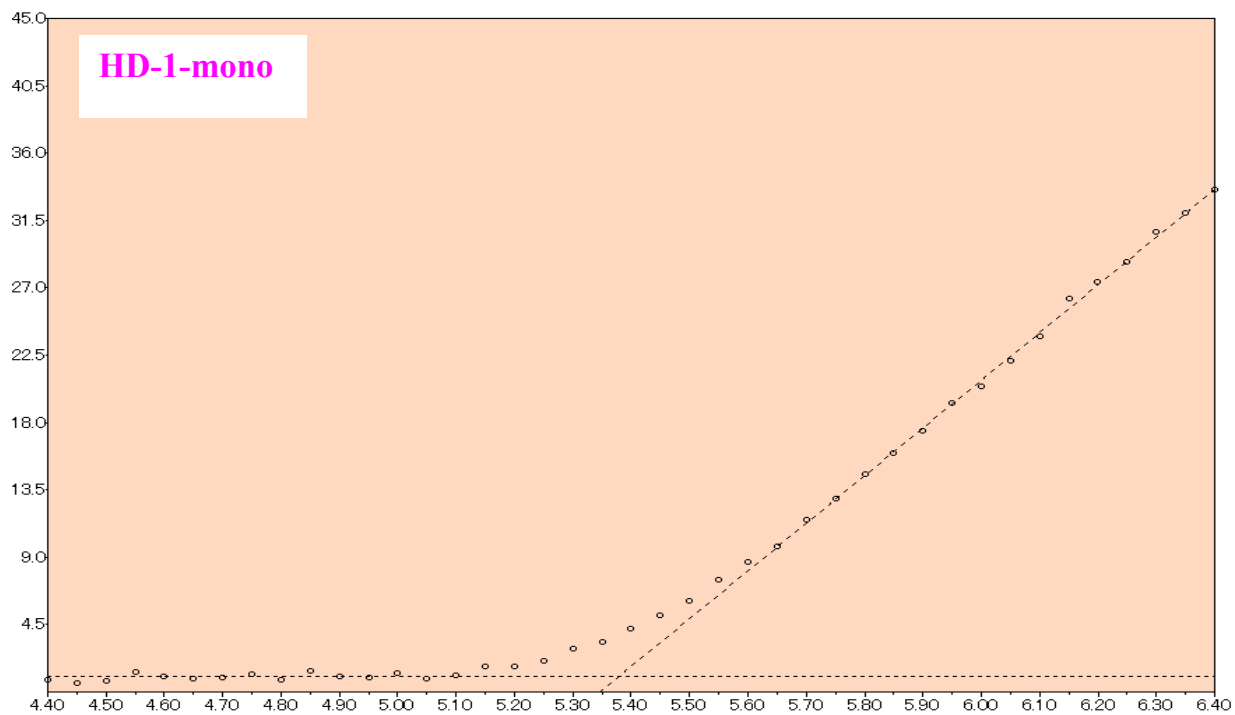
The experimental HOMO and  $E_{0-0}$  energy values for HD-1-mono was measured using a photoemission yield spectrometer and the experimental absorption/emission spectra point of overlap, respectively, and the procedure was described in detail elsewhere<sup>4</sup>. The onset of oxidation were measured in DMF with 0.1 M [TBA][PF<sub>6</sub>] and with a scan rate of 50 mV/s. Glassy carbon was used as the working electrode (WE), Pt wire as counter electrode and Ag/Ag<sup>+</sup> in acetonitrile was used as the reference electrode. It was calibrated with Fc/Fc<sup>+</sup> as an internal standard and converted to NHE by addition of 0.63 V. Figure 5-6S shows the CV results and 7S shows the AC3 results of HD-1-mono.



**Figure 5S.** HOMO CV results energy level of HD-1-mono (-5.46eV)

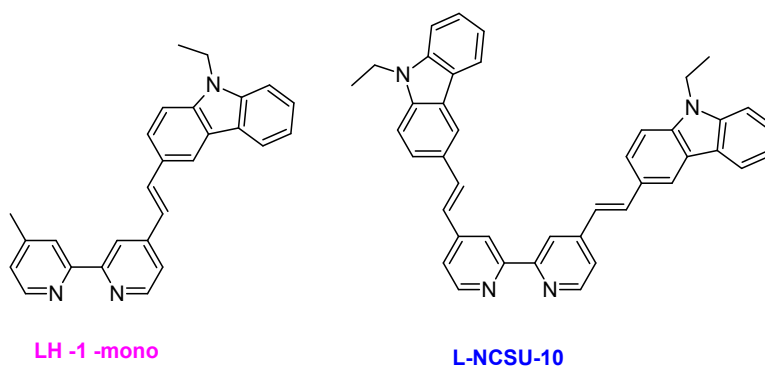


**Figure 6S.** HOMO CV results energy level of NCSU-10 (-5.5eV)

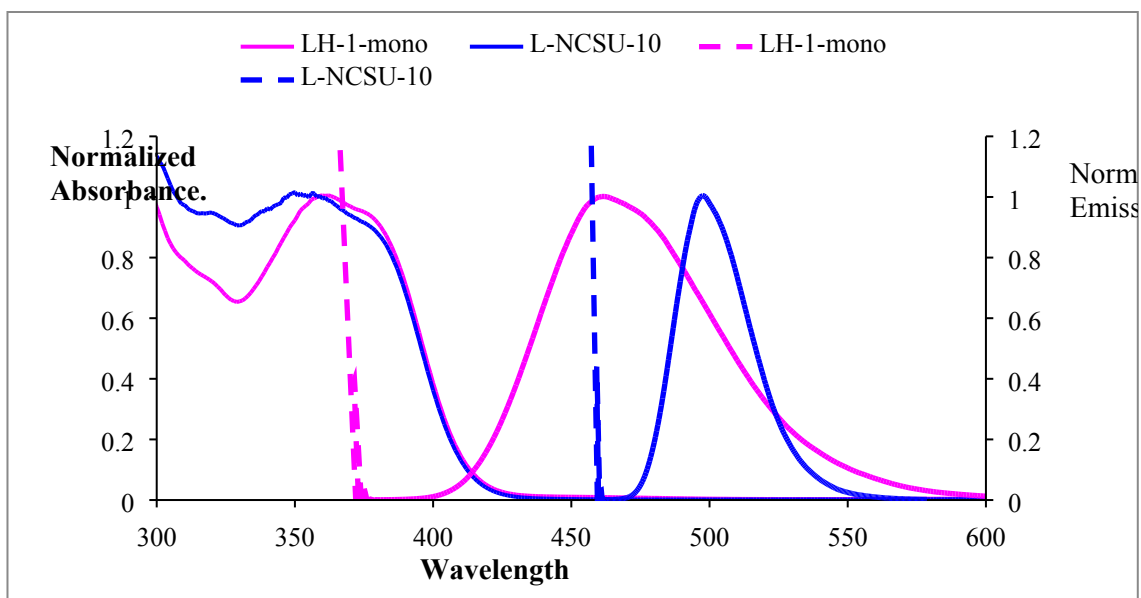


**Figure 7S.** AC3 HOMO energy of HD-1-mono (-5.38eV)

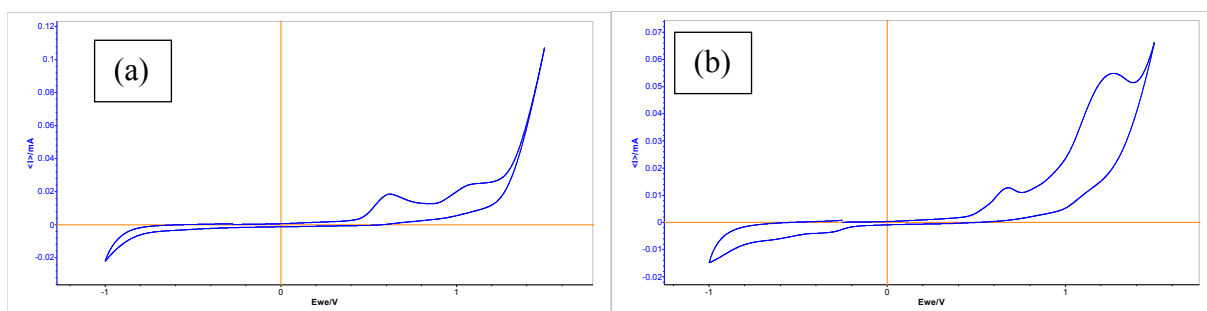
## 2.7 Ligands Characterization



**Figure 8S.** Structures of LH-1-mono and L-NCSU-10



**Figure 9S.** Absorption (solid line) and emission (dotted line) comparison of LH-1-mono and L-NCSU-10



**Figure 10S.** CV graphs (a) LH-1-mono and (b) L-NCSU-10

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

A double-layer TiO<sub>2</sub> photoelectrode (10+5)  $\mu\text{m}$  in thickness with a 10  $\mu\text{m}$  thick nanoporous layer and a 5  $\mu\text{m}$  thick scattering layer (area: 0.25 cm<sup>2</sup>) were prepared using a reported method <sup>5</sup>. Fluorine doped tin oxide-coated glass electrodes (Nippon Sheet Glass Co., Japan) with a sheet resistance of 8-10  $\text{ohm}^{-2}$  and an optical transmission of greater than 80% in the visible range were screen printed using anatase TiO<sub>2</sub> colloids (particle size  $\sim$ 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<sup>6</sup>. The dye solutions ( $2 \times 10^{-4}$  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<sub>2</sub> surface.

### **3.2. 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 Syrlyn 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 0.5 M TBP in acetonitrile.

## **4. Photoelectrochemical Measurements**

### **4.1. 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>).

### **4.2. 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 1, 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><sup>7</sup>.

$$IPCE(\lambda) = 1240 \left( \frac{I_{SC}}{q\lambda P_0} \right) \quad \text{Equation 1}$$

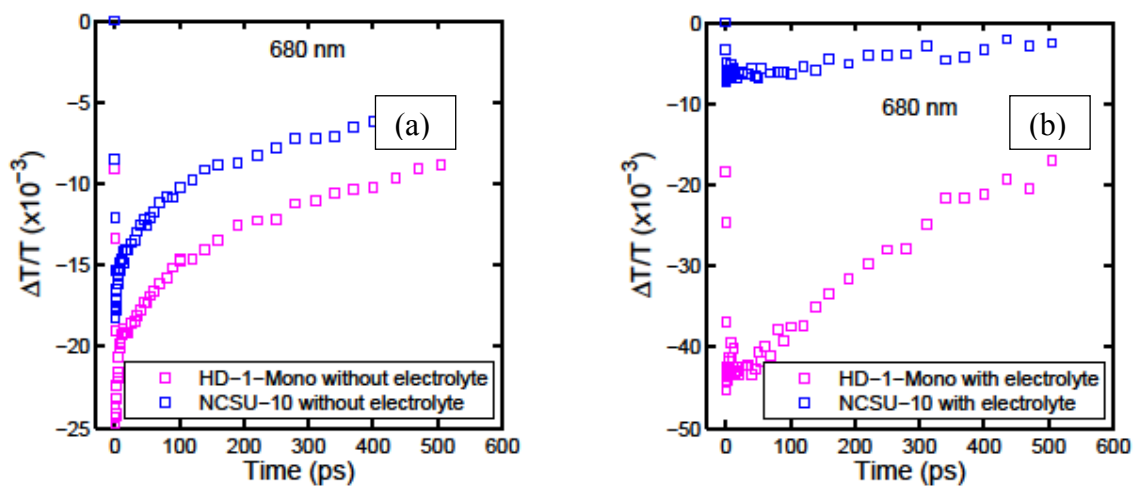
The incident photon-to-current conversion efficiency was plotted as a function of wavelength.

### 4.3. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer with a potentiostat (Bio-Logic SP-150) under illumination using a solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). EIS spectra were recorded over a frequency range of 100 mHz to 200 kHz at 298 K. The applied bias voltage and AC amplitude were set at the  $V_{oc}$  of the DSCs, with AC amplitude was set at 10mV. The electrical impedance spectra were fitted using Z-Fit software (Bio-Logic). The DSC's used for impedance measurements were prepared by using the method reported elsewhere<sup>8</sup>.

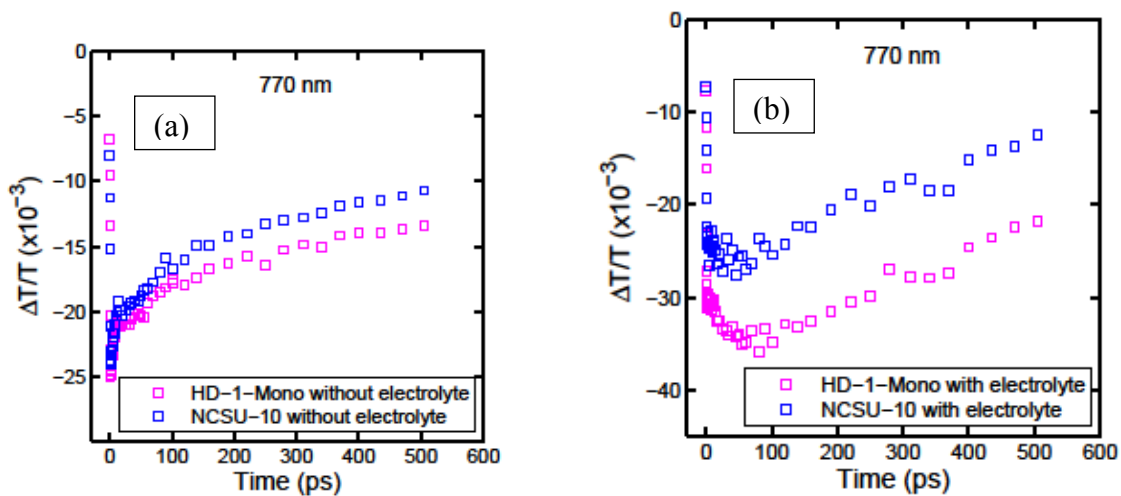
### 5. Transient Absorption Spectroscopy

For transient absorption experiments the samples were excited with 100 fs pulses tuned at 530 nm and evolution of the absorption at different time delays was measured by using a 300 fs white-light continuum pulses that span from 500 nm to 800 nm in the spectra. These measurements were carried in transmission mode. The DSSC which were used for these studies were prepared by first squeeze printing the transparent TiO<sub>2</sub> nanoparticles (active area 0.49cm<sup>2</sup>) on clean glass slides followed by annealing at 450C for 1hr. These electrodes were then dipped in dye solution ( $2 \times 10^{-4}M$ ) facing up for two hours at room temperature. After two hours these electrodes were taken out of the dye solution and sandwiched with microscope slides covering the active area. Electrolyte was latter introduced between the two interfaces.

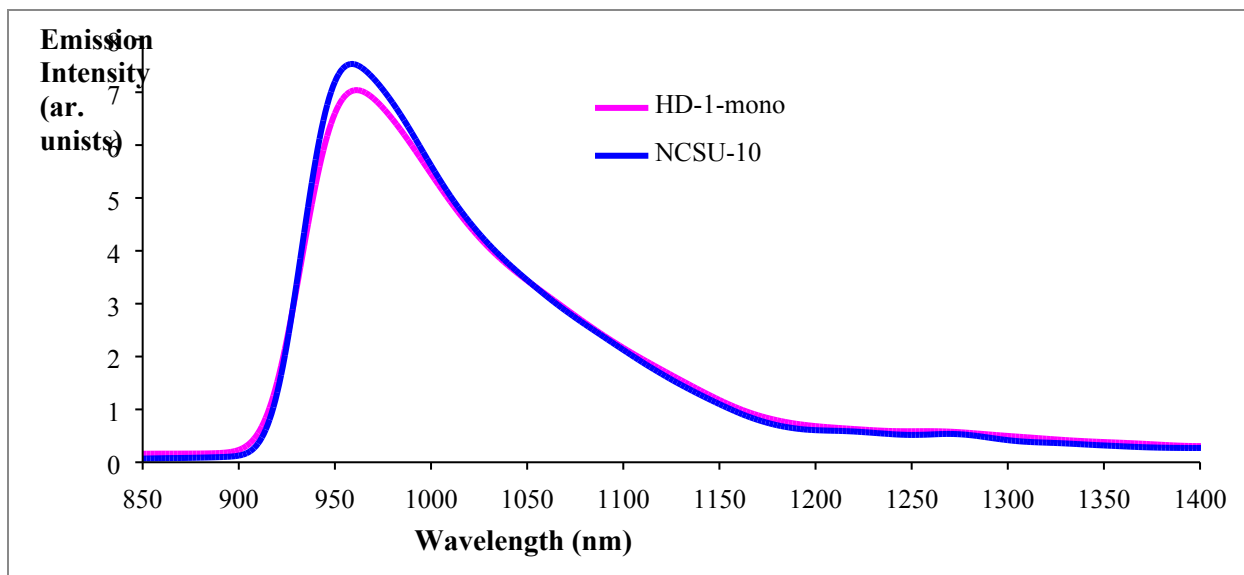


F

**figure 11S.** PIA decay dynamics of (a) HD-1-Mono and NCSU-10 without electrolyte (b) with electrolyte at 680 nm. Colors are indicated in the legend.



**Figure 12S.** PIA decay dynamics of (a) HD-1-Mono and NCSU-10 without electrolyte (b) with electrolyte at 770 nm. Colors are indicated in the legend.



**Figure 13S.** Phosphorescence graph of HD-1-mono and NCSU-10



## REFERENCES

1. El-Shafei, A.; Hussain, M.; Atiq, A.; Islam, A.; Han, L. *J. Mater. Chem.* **2012**, *22*, 24048-24056.
2. El-Shafei, A.; Hussain, M.; Islam, A.; Han, L. *J. Mater. Chem. A* **2013**, *1*, 13679-13686.
3. Garelli, N.; Vierling, P. *J. Org. Chem.* **1992**, *57*, 3046-3051.
4. Islam, A.; Sugihara, H.; Hara, K.; Singh, L. P.; Katoh, R.; Yanagida, M.; Takahashi, Y.; Murata, S.; Arakawa, H.; Fujihashi, G. *Inorg. Chem.* **2001**, *40*, 5371-5380.
5. Nazeeruddin, M. K.; Splivallo, R.; Liska, P.; Comte, P.; Gratzel, M. *Chem. Commun.* **2003**, *0*, 1456-1457.
6. Wang, Z.; Yamaguchi, T.; Sugihara, H.; Arakawa, H. *Langmuir* **2005**, *21*, 4272-4276.
7. Islam, A.; Chowdhury, F. A.; Chiba, Y.; Komiya, R.; Fuke, N.; Ikeda, N.; Nozaki, K.; Han, L. *Chem. Mater.* **2006**, *18*, 5178-5185.
8. Ito, S.; Murakami, T. N.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin, M. K.; Grätzel, M. *Thin Solid Films* **2008**, *516*, 4613-4619.