Stable and Efficient Carbazole-Based Amphiphilic Ru (II) Sensitizers for Dye-Sensitized Solar Cells

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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 spectrometry Analysis was carried out on a high resolution mass spectrometer – the Thermo Fisher Scientific Exactive Plus MS, a benchtop full-scan OrbitrapTM mass spectrometer using Heated Electrospray Ionization (HESI). Samples were dissolved in methanol and sonicated for 15 minutes. They were then diluted 1:1 with 20mM ammonium acetate and analyzed via syringe injection into the mass spectrometer at a flow rate of 10 μL/min. The mass spectrometer was operated in negative ion mode. 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.). ¹H-NMR spectra were recorded in a Bruker 500 MHz or Varian 400MHz spectrometer.

1. Synthesis of ligands

1.1. Synthesis of 4, 4-bis((E)-2-(9-heptyl-9Hcarbazol-3-yl)vinyl)-2,2-bipyridine (LH-14)

Before the synthesis of LH-14, 9-heptyl-9H-carbazole and 9-heptyl-9H-carbazole-3-carbaldehyde was synthesized by following the previously reported procedures ¹, ². General procedure for the synthesis of ligands is given in Scheme1. The antenna ligand LH-14 was synthesized under pressure in a glass tube containing 4,4'-dimethyl-2,2'-bipyridine (0.92g, 5mmol), 9-heptyl-9H-carbazole-3-carbaldehyde (2.93g, 10mmol), 3.8ml of chlorotrimethylsilane (30mmol), and a magnetic stirrer bar in 50ml of anhydrous DMF ³, ⁴. 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 48 hours, the color of the reaction mixture changed to dark 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-14. It was then dried for overnight at 50 °C to obtain 82% yield. LH-14 was used for next step without further purification.

1.2. Synthesis of 4,4-bis((E)-2-(9-octadecyl-9H-carbazol-3-yl)vinyl)-2,2-bipyridine (LH-15)
Similar procedure was used to synthesize LH-15 in 80% yield as used for LH-14, except in the pressure tube reaction chlorotrimethylsilane was used in excess along with at 130°C instead of 100°C for 48hrs.

![Scheme S1 Synthesis of Ligands LH-14 and LH-15](image)

1.3. Synthesis of 2, 2′-Bipyridinyl-4, 4′-dicarboxylic acid
The 2, 2′-Bipyridinyl-4, 4′-dicarboxylic acid was synthesized according to published procedure. 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 (Na₂Cr₂O₇) (10.9 g, 36.5 mmol) in concentrated sulfuric acid (H₂SO₄) (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 % aqueous sodium hydroxide. The product was crystallized by slowly acidifying the solution with 10 % aqueous 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%).

1.4. Synthesis of HD-14

A general procedure for the synthesis of dyes is shown in Scheme 2. The synthesis of HD-14 was carried out in a one-pot three-step reaction procedure. 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, dichloro-(p-cymene)-Ruthenium (II) dimer (0.15g, 0.2mmol) and LH-14 (0.35g, 0.4mmol). The reaction mixture was stirred at 90°C for 4h. Then, 2,2’-bipyridyl-4,4’-dicarboxalic acid was added (0.1g, 0.4mmol) and the temperature was raised to 140°C and allowed to run for 5 hours, the color of reaction mixture changed from dark yellow to dark green in this step. After the 5 hours, excess of NH₄NCS (0.3g) was added to the reaction mixture, and the reaction mixture was allowed to run for extra 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 0.5g (88%) of crude product was collected.

After drying, HD-14 was dissolved in methanol with the addition of Tetrabutylammonium hydroxide (TBAOH). HD-14 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 in the refrigerator, precipitate was filtered, washed with
plenty of de-ionized water to bring pH to neutral. The pure dye was then dried overnight and collected (0.25g, 45%). The pure dye was then further analyzed by ATR/FT-IR, $^1$H NMR and high resolution mass spectrometry. HD-14 was characterized by ESI high resolution MS and $^1$HNMR, which is given in coming sections.

1.5. Synthesis of HD-15

Similar synthetic route and purification procedure was used to synthesize HD-15 in 40 % yield of pure dye after running through Sephadex LH-20 column three times. HD-15 was characterized by $^1$HNMR, which is given in coming sections.
2. ANALYTICAL MEASUREMENTS

2.1. UV-Visible spectra

UV-Visible spectra of HD-14 and HD-15 were measurement 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. 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 S1 to S8 show the FT-IR of starting material, ligands and dyes in pure form, respectively.

Figure S1. ATR/FT-IR of 9-heptyl-9H-carbazole
Figure S2. ATR/FT-IR of 9-heptyl-9H-carbazole-3-carbaldehyde

Figure S3. ATR/FT-IR of 4,4-bis((E)-2-(9-heptyl-9Hcarbazol-3-yl)vinyl)-2,2-bipyridine (LH-14)
Figure S4. ATR/FT-IR of 9-octadecyl-9H-carbazole

Figure S5. ATR/FT-IR of 9-octadecyl-9H-carbazole-3-carbaldehyde
Figure S6. ATR/FT-IR of 4,4-bis((E)-2-(9-octadecyl-9H-carbazol-3-yl)vinyl)-2,2-bipyridine (LH-15)

**HD-14**: 2101.3 cm\(^{-1}\) (-NCS stretch, N-bonded isomer, very strong); 1719.9 cm\(^{-1}\) (C=O stretch of -COOH); 2928.3 cm\(^{-1}\) (C-H stretch of alkyl chain).

**HD-15**: 2101.1 cm\(^{-1}\) (-NCS stretch, N-bonded isomer, very strong); 1720.1 cm\(^{-1}\) (C=O stretch of -COOH); 2923.7 cm\(^{-1}\) (C-H stretch of alkyl chain, stronger than for HD-14).
Figure S7. ATR/FT-IR of HD-14

Figure S8. ATR/FT-IR of HD-15

2.3. Mass spectrometry

**Figure S11.** ESI mass spectrum of HD-14, Mass 1196.338600; [M - 1H]$^-$; Theo. M/Z = 1195.33062, Found. M/Z 1195.33400, Error = 2.83 ppm.

**Figure S12.** ESI mass spectrum of HD-15, Mass 1503.0196; Found [M - 2(C$_{18}$H$_{37}$) + NH$_4$COOCH$_3$-H]$^-$. 
2.4. $^1$H-NMR spectroscopy

$^1$H-NMR spectra were recorded in DMSO at room temperature using a Varian 400 MHz for ligands and Bruker 700 MHz spectrometer for dyes. 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.

$^1$H-NMR, LH-14, (400 MHz, Chloroform-d) $\delta$ 9.06 (s, 1H), 8.73 (d, J = 9.0 Hz, 1H), 8.12 (s, 2H), 8.03 (s, 2H), 7.83 – 7.72 (m, 4H), 7.60 (s, 2H), 7.52 – 7.37 (m, 6H), 7.33 (s, 4H), 7.22 (d, J = 17.2, 2H), 4.35 (s, 4H), 2.64 (s, 2H), 1.88 (q, J = 7.5, 6.8 Hz, 4H), 1.36 (s, 4H), 1.25 (s, 10H), 0.86 (t, J = 5.6 Hz, 6H).

$^1$H-NMR, HD-14, (700 MHz, DMSO-$d_6$) $\delta$ = $\delta$ 9.46 (s, 1H), 9.24 (s, 1H), 8.97 (s, 1H), 8.9 (s, 1H), 8.85-8.75 (s, 2H), 8.63 (d, J = 16.4 Hz, 1H), 8.5 (s, 1H), 8.45 (s, 1H), 8.20 (d, J=26.5, 7.2, 1H), 7.99 – 7.89 (m, 4H), 7.77 (dt, J=16.2, 8.5, 4H), 7.72 – 7.45 (m, 10H), 7.44 – 7.21 (m, 2H), 4.44 (dd, J=32.7, 8.6, 4H), 3.00 (s, 1H), 2.60 (d, J=3.8, 1H), 2.52 (s, 1H), 2.40 (s, 1H) 1.85 – 1.76 (m, 4H), 1.26 – 1.15 (m, 12H), 0.82 (dtd, J=19.5, 7.1, 4.2, 6H).

$^1$H-NMR, LH-15, (400 MHz, Chloroform-d) $\delta$ 8.97 (d, J=34.1, 1H), 8.74 (d, J=5.7, 2H), 8.39 (d, J=11.4, 1H), 8.27 – 7.95 (m, 4H), 7.76 (d, J=17.0, 2H), 7.49 (s, 14H), 4.47 – 4.18 (m, 4H), 2.78 (s, 2H), 1.90 (s, 2H), 1.27 (d, J=16.6, 60H), 0.88 (t, J=8.0, 6H).

$^1$H-NMR, HD-15 (700 MHz, DMSO-$d_6$) $\delta$ = 9.45 (s, 1H), 9.13 (d, J=5.8, 1H), 9.08 (d, J=5.6, 2H), 8.98 (d, J=1.8, 1H), 8.92 (s, 1H), 8.83 (d, J=10.1, 1H), 8.65 (s, 1H), 8.56 (d, J=1.6, 1H), 8.44 (d, J=1.6, 1H), 8.36 – 8.28 (m, 1H), 8.23 (d, J=7.6, 1H), 8.20 – 8.13 (m, 1H), 8.11 – 8.04 (m, 1H), 7.96 – 7.88 (m, 2H), 7.88 – 7.84 (m, 1H), 7.80 – 7.71 (m, 2H), 7.65 (ddd, J=10.7, 7.8, 3.0, 3H), 7.62 (d, J=8.2, 1H), 7.57 – 7.45 (m, 2H), 7.39 (d, J=6.0, 1H), 7.34 (d, J=5.8, 1H), 7.31 –
7.22 (m, 2H), 7.10 (d, J=5.8, 1H), 4.42 (t, J=7.3, 4H), 2.74 (s, 1H), 2.46 (s, 1H), 1.79 (t, J=6.8, 4H), 1.19 (t, J=19.8, 60H), 0.84 (d, J=2.1, 1H), 0.83 (d, J=2.2, 2H), 0.81 (d, J=2.2, 1H).

2.5. Cyclic Voltammetry Results

The experimental HOMO and E0-0 energy values for HD-14 and HD-15 were measured by cyclic voltammetry and the experimental absorption/emission point of overlap, respectively. The onset of oxidation were measured in DMF with 0.1 M [TBA][PF6] 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/AgCl in acetonitrile was used as the reference electrode. It was calibrated with Fc/Fc$^+$ as an internal standard and converted to NHE by addition of 0.63 V. Figures 13S and 14S show the HOMO energies of HD-14, and HD-15, respectively.

![HD-14 CV graph](image)

**Figure 13S.** CV graph of HD-14 (-5.45eV)
2.6. Time Correlated Single Photon Counting (TCSPC) Measurements

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 0.1 sec.

In the case of lifetime measurements, time-correlated single photon counting method was employed on solution of dyes in DMF by exciting the samples using a pulse laser (460 nm, NanoLED) at a 1 MHz repetition rate with band pass of 15 nm. 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). The lifetime decay spectra were then fitted with DAS (data analysis software) from Horiba Scientific.

3. CELL PREPARATIONS AND PHOTOVOLTAIC CHARACTERIZATIONS

3.1. 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 6. 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 7. 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.

3.2. 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 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 0.5 M TBP in acetonitrile.

3.3. 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$^{-2}$).
3.4. 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 (mA cm$^{-2}$) 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$^{-2}$.

Equation (1)

$$IPCE(\lambda) = \frac{1240 I_{SC}}{q \lambda P_0}$$

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

3.5. Electrochemical Impedance Spectroscopy (EIS)

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 $V_{oc}$ of the DSCs. The applied bias voltage and AC amplitude were set at the $V_{oc}$ of the DSCs. The electrical impedance spectra were characterized using Z-View software (Solartron Analytical).
3.6. Effect of additives and coadsorbate

Figure 15S. Photocurrent action spectra (IPCE) obtained with (a) HD-14 and (b) HD-15, anchored on nanocrystalline TiO$_2$ film with additive TBP and coadsorbate DCA (20mM).
Figure 16S. Photocurrent-voltage characteristics of DSSCs sensitized with the complexes (a) HD-14 and (b) HD-15 Electrolyte, 0.6 M DMPII, 0.1 M LiI, 0.05 I\(_2\) in acetonitrile (AN), with additive TBP and coadsorbate DCA (20mM).

3.7. Long Term Stability Test

A close system as shown in Figure S17 was used for the long term stability test for 1000hrs under light soaking with AM 1.5 illumination (light intensity: 100 mW cm\(^{-2}\)). A 420-nm cut-off filter was applied during illumination. Ionic-liquid electrolyte 0.15 M I\(_2\), 0.1 M GuSCN, 0.5 M MBI, and 1 M PMII in MPN at 25 °C. during light illumination was employed. The actual temperature inside the cell was around 45-50 °C due to heat generated from irradiation.

Figure S17. Closed system used for doing long term stability test

3.8. Transient absorption Laser Flash photolysis experiment spectroscopy

The transient absorption spectroscopy study was carried out using an Edinburgh Instrument nanosecond laser flash photolysis spectrometer (LP920). The LP920 was associated with a
Continuum Nd-YAG laser (Surelite; 10 Hz repetition rate; FWHM 5 ns) through a Surelite optical parametric oscillator. The beam was expanded by a planoconcave lens in order to irradiate the sample at a large cross section (more than 1 cm²). The samples were oriented at 45° angle to both excitation and probe beams. Transparent mesoporous TiO₂ samples (thicknesses 6-12 μm) coated on glass substrates were dyed by adsorption of the HD-14-HD-15 complexes for 15 min as well as for comparison by N719 dye (overnight). Two drops of LiI/I₂ electrolyte were sandwiched between the samples and a thin microscope cover glass (where necessary). A low-intensity laser beam (≤ 6 mJ cm⁻²) was used for the flash photolysis. The dye was excited at 500 nm and transient absorption spectrum was recorded at probe light wavelength of 560 nm where bleaching of excited-state dye occurs. Signal-to-noise ratio was improved via 100 laser shots.

3.9. Femtosecond 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 DSC which were used for these studies were prepared by first squeeze printing the transparent TiO₂ nanoparticles (active area 0.49cm²) on clean glass slides followed by annealing at 450°C for 1hr. These electrodes were then dipped in dye solution (2*10⁻⁴M) 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 later introduced between the two interfaces.
Figure S18. Transient absorption dynamics of HD-14, HD-15, and N719 at 760 nm without the addition of the electrolyte.
REFERENCES


