A femtosecond study of the anomaly in electron injection for dye-sensitized solar cells: Influence of isomerization employing Ru (II) sensitizers with anthracene and phenanthrene ancillary ligands

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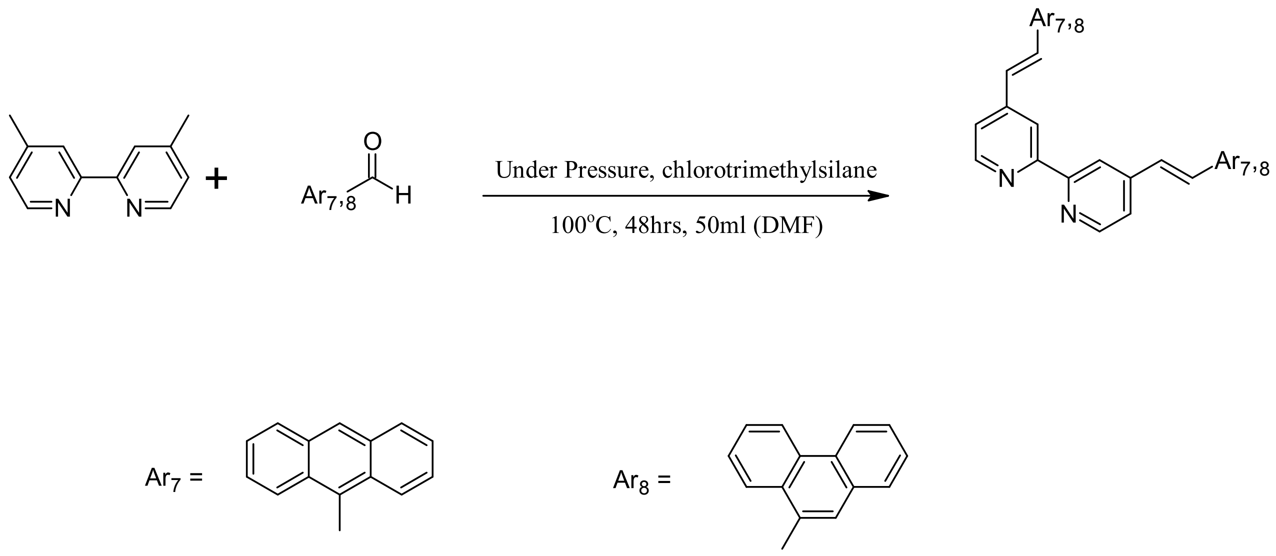
1. Materials and Equipment

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.). ^{1}H-NMR spectra were recorded using a Bruker 500 MHz or Varian 400MHz spectrometer.

2. Chemical Synthesis

2.1. Synthesis of Ancillary Ligands

General procedure for the synthesis of ligands is given in Scheme1 (Supplemental information).The antenna ligand LH-7 was synthesized under pressure in a glass tube containing 4,4'-dimethyl-2,2'-bipyridine (0.7g, 3.6mmol), 9-anthracenecarbaldehyde (1.5g, 7.3mmol), 2.8ml of chlorotrimethylsilane (22mmol), and a magnetic stirrer bar in 50ml of anhydrous DMF [1, 2]. Once the tube was closed with the cap the reaction temperature was raised to 100 ^{o}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 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 hexane in sequence to obtain LH-7. It was then dried for overnight at 50 ^{o}C to obtain 87% yield. LH-7 was used for next step without further purification. LH-8 was synthesized following the same procedure.



LH-7

LH-8

Scheme S1. Synthesis of Ligands LH-7 and LH-8

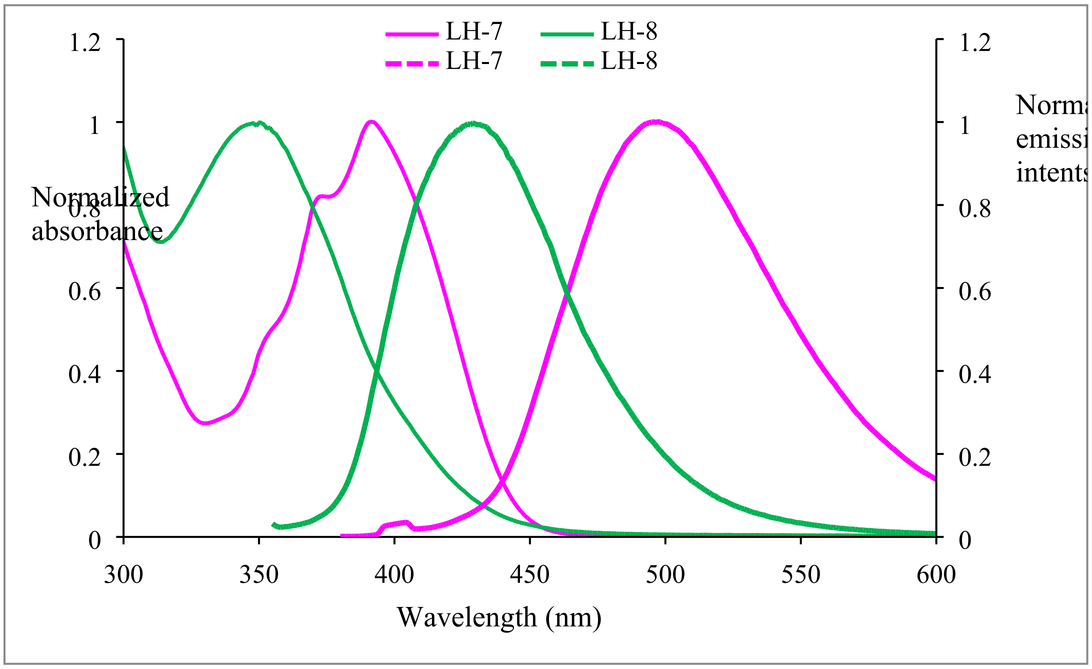


Figure S1. Absorption (solid line) and emission (dotted line) comparison of LH-7 and LH-8

^{1}H-NMR, LH-7 ($CDCl_3$-d): δ = 9.55 (s, 1H), 9.01 (t, J=1.0, 1H), 8.98 (t, J=1.0, 1H), 8.93 (s, 1H), 8.90 (s, 1H), 8.85 (s, 1H), 8.79 (s, 1H), 8.72 (s, 2H), 8.57 (d, J=8.9, 1H), 8.47 (s, 1H), 8.39 (d, J=8.8, 2H), 8.09 (s, 2H), 8.06 (s, 2H), 8.04 (s, 1H), 8.02 (s, 1H), 7.71 (s, 1H), 7.68 (s, 1H), 7.67 (s, 1H), 7.57 (s, 1H), 7.55 (s, 2H), 7.54 (s, 1H), 7.51 (s, 1H), 7.49 (s, 1H).

^{1}H-NMR, LH-8 (DMSO-d_6): δ = 8.97 (s, 2H), 8.90 (s, 1H), 8.88 (s, 2H), 8.79 (d, J=5.4, 1H), 8.72 (s, 1H), 8.68 (s, 1H), 8.52 (s, 2H), 8.38 (s, 1H), 8.35 (s, 1H), 8.15 (d, J=1.5, 1H), 8.13 (s, 1H), 8.11 (s, 1H), 8.09 (s, 1H), 7.81 (s, 1H), 7.81 (s, 2H), 7.79 (s, 1H), 7.73 (s, 2H), 7.68 (s, 1H), 7.66 (s, 1H), 7.62 (s, 1H), 7.57 (s, 1H).

2.2. Synthesis of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid

The 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid was synthesized according to published procedure [3]. 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 ($Na_2Cr_2O_7$) (10.9g, 36.5 mmol) in concentrated sulfuric acid (H_2SO_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 % aquous sodium hydroxide. The product was crystallized by slowly acidifying the solution with 10 % aquous hydrochloric acid at a pH of 2. The precipitation and acidification process was repeated three times to obtain white chromium free precipitates of 2, 2'-Bipyridinyl-4, 4'-dicarboxylic acid (2.56g, 90%).

2.3. Synthesis of HD-7

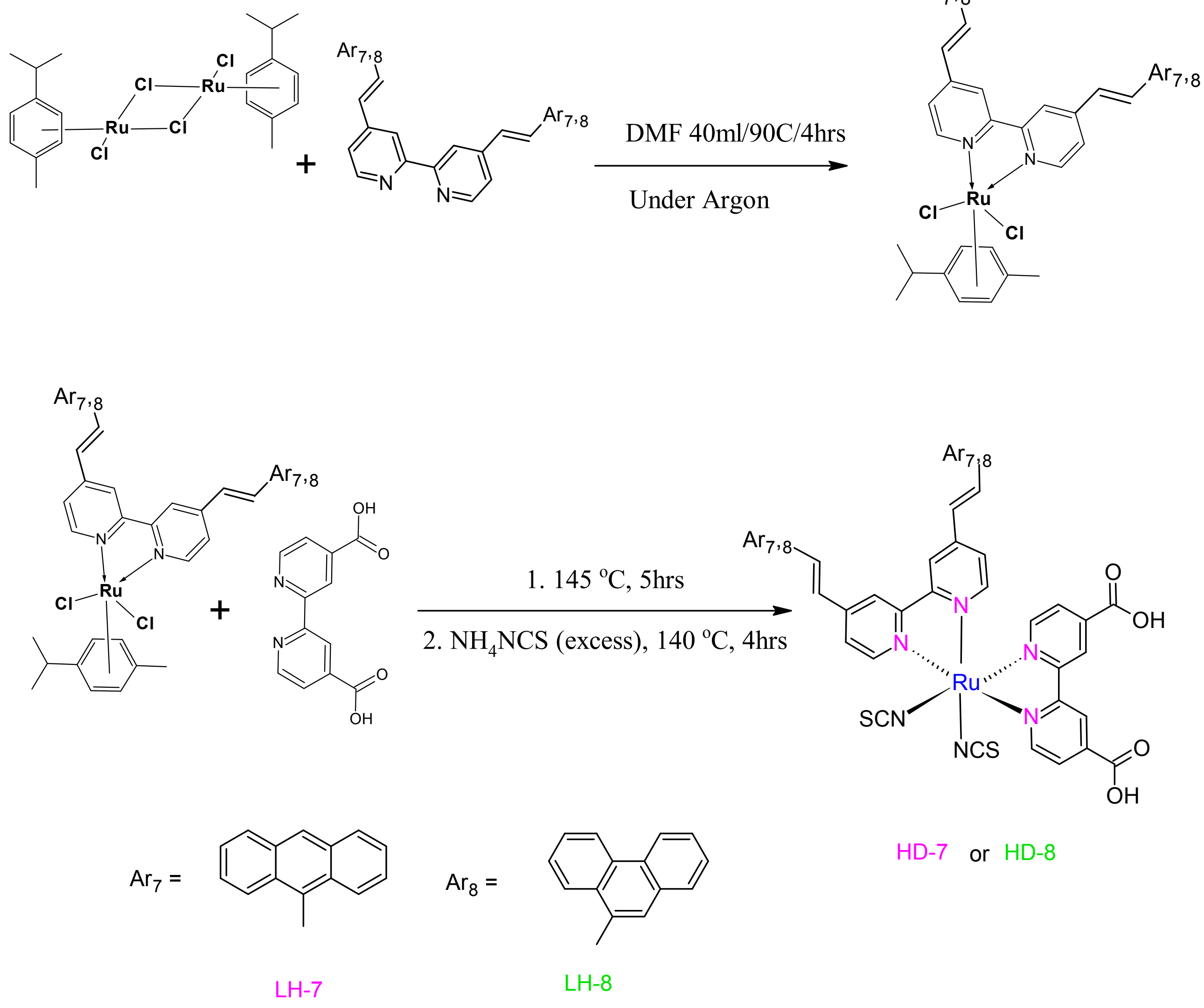
A general procedure for the synthesis of dyes is shown in Scheme S2.The synthesis of HD-7 was carried out in a one-pot three-step reaction procedure. The reactions were carried out in a 150 ml reaction flask equipped with a condenser and magnetic stirrer bar under argon. The flask was charged with anhydrous DMF, dichloro-(p-cymene)-Ruthenium (II) dimer (0.163g, 0.3mmol) and LH-7 (0.3g, 0.5mmol). The reaction mixture was stirred at 90°C for 4h. Then, 2,2'-bipyridyl-4,4'-dicarboxalic acid was added (0.13g, 0.5mmol) and the temperature was raised to 145°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

NH_4NCS (0.35g) 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 of crude product was collected.

After drying, HD-7 was dissolved in methanol with the addition of Tetrabutylammonium hydroxide (TBAOH). HD-7 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, 55%). The pure dye was then further analyzed by ATR/FT-IR, ^1H NMR and high resolution mass spectrometry.

2.4 Synthesis of HD-8

Similar synthetic route and purification procedure was used to synthesize HD-8 in 50 % yield of pure dye after running through Sephadex LH-20 column three times.



Scheme 2. Synthetic route for HD-7 and HD-8

^{1}H-NMR, HD-7 (DMSO-d_6): δ = 9.44 (s, 1H), 9.35 – 9.29 (m, 1H), 9.26 (d, J=5.9, 1H), 9.06 (s, 2H), 8.91 (td, J=16.4, 5.7, 3H), 8.71 – 8.65 (m, 3H), 8.62 (d, J=13.9, 1H), 8.53 (d, J=8.7, 2H), 8.35 (dd, J=10.1, 4.8, 3H), 8.30 (d, J=5.9, 1H), 8.18 (dd, J=15.2, 8.3, 2H), 8.14 – 8.12 (m, 1H), 7.66 (d, J=2.6, 1H), 7.63 (s, 1H), 7.62 (s, 1H), 7.60 (s, 1H), 7.56 (d, J=2.0, 1H), 7.55 (s, 1H), 7.54 (s, 1H), 7.53 (s, 1H), 7.52 (d, J=3.3, 1H), 7.39 – 7.27 (m, 2H), 7.15 – 7.07 (m, 1H), 7.03 (d, J=16.1, 1H). FT-IR: 2100.5 cm^{-1} (-NCS stretch, N-bonded isomer, very strong); 1720.4 cm^{-1}

(C=O stretch of -COOH). ESI mass spectrum: [M - 1H] $^{-1}$; Theo. M/Z = 1021.12102, Found. M/Z =1021.12492, Error = 3.822ppm.

^{1}H-NMR, HD-8 (DMSO-d_6): δ 9.44 (s, 1H), 9.27 (d, J = 7.0 Hz, 1H), 9.22 (s, 1H), 9.17 (s, 1H), 9.10 (d, J = 5.6 Hz, 1H), 9.07 (s, 1H), 9.03 (s, 1H), 8.91 (s, 4H), 8.86 – 8.84 (m, 2H), 8.71 (s, 1H), 8.44 (s, 1H), 8.40 (s, 1H), 8.25 (s, 1H), 8.15 (s, 1H), 7.86 – 7.82 (m, 4H), 7.73-7.60 (dd, J = 22.3, 15.6 Hz, 12H), 7.48 (s, 1H), 7.39 (s, 1H). 2103.3 cm^{-1}. FT-IR: (-NCS stretch, N-bonded isomer, very strong); 1719.5 cm^{-1} (C=O stretch of -COOH). ESI mass spectrum: [M - 1H] $^{-1}$; Theo. M/Z = 1021.12102, Found. M/Z 1021.12464, Error = 3.547ppm.

3. ANALYTICAL MEASUREMENTS

3.1. UV-Visible spectra

UV-Visible spectra of HD-7 and HD-8 were measurement using a concentration of 2.0 X 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.

3.2. Fluorescence Spectra

Fluorescence spectra were recorded in a 1 cm path length quartz cell using 2 *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 λ_{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 single photon counting method was employed on solution of dyes in DMF by exciting the samples 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). Ludox was used as a scattering solution to measure the prompt for instrument response function. The lifetime decay spectra were then fitted with DAS (data analysis software) from Horiba Scientific. TCSPC studies on dye films were carried out using the similar method with angle of 60° to the pulse laser (460nm, NanoLED) of the solid sample holder.

All of the decay curves were fitted with 2-exponential showing the multiexponental decay behavior having fast (shorter lifetime) and slow (longer lifetime) components. However, the relative amplitude of the fast component (B1 in S1) for all of the dyes was too small and can be ignored.

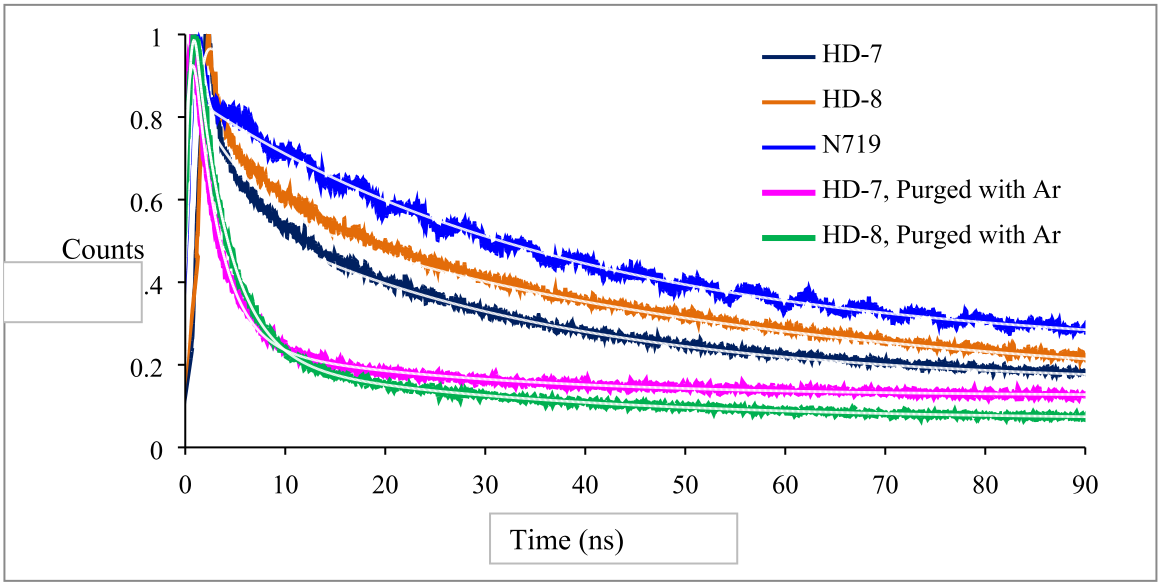


Figure S2. Excited state decay behavior of HD-7, HD-8, and N719 dissolved in DMF, smooth lines corresponds to the fits of the experimental data after convolution with the instrument response.

Table S1. Excited state lifetime in DMF solution

Sample Name	τ/ ns(T1)	τ/ ns (T2)
HD-7	2	31

	(*B1=8)	(B2=92)
HD-8	5 (B1=6)	51 (B2=94)
N719	0.1 (B1=3)	38 (B2=97)
HD-7, Purged with Ar	3 (B1=44)	25 (B2=56)
HD-8, Purged with Ar	3 (B1=42)	30 (B2=58)

*B denotes the relative amplitude of each component

3.3. 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 4cm^{-1}. The complexes and intermediates were characterized using the same parameters. Figures 1S and 2S show the FT-IR of HD-7 and HD-8, respectively.

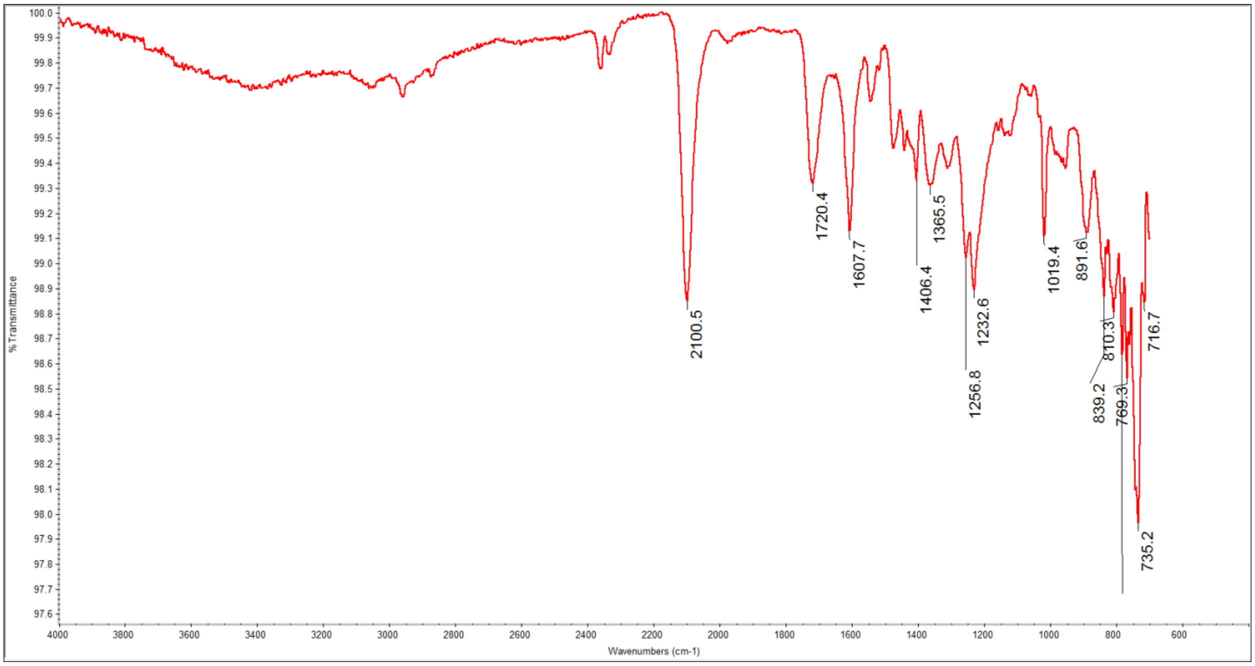


Figure S3. ATR/FT-IR of HD-7

HD-7: 2100.5 cm^{-1} (-NCS stretch, N-bonded isomer, very strong); 1720.4 cm^{-1} (C=O stretch of -COOH).

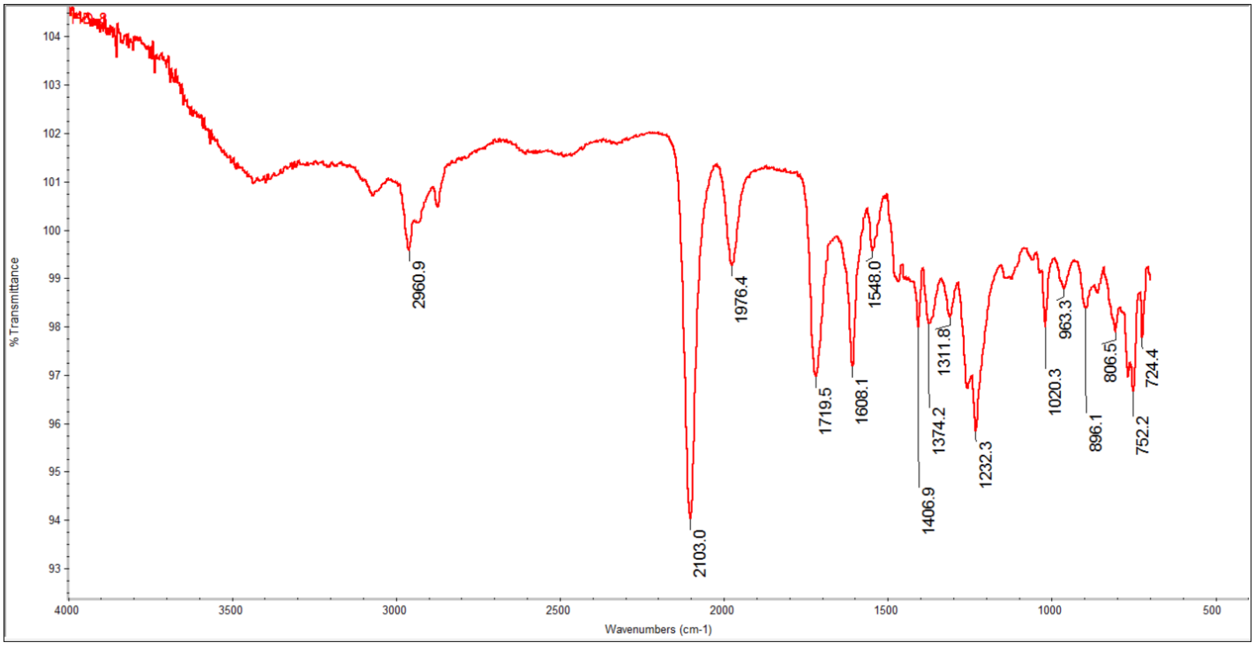


Figure S4. ATR/FT-IR of HD-8

HD-8: 2103.3 cm^{-1} (-NCS stretch, N-bonded isomer, very strong); 1719.5 cm^{-1} (C=O stretch of -COOH).

3.4. High Resolution Mass spectrometry

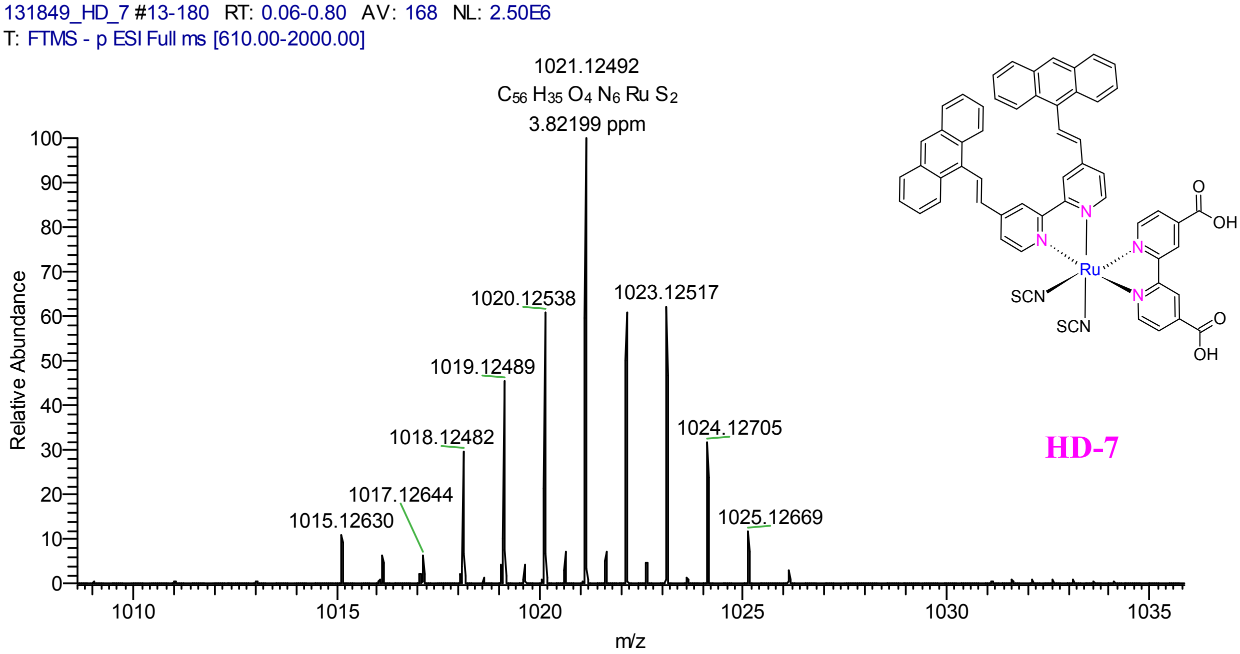


Figure S5. ESI mass spectrum of **HD-7**, [M - 1H]$^{-1}$; Theo. M/Z = 1021.12102, Found. M/Z 1021.12492, Error = 3.822ppm.

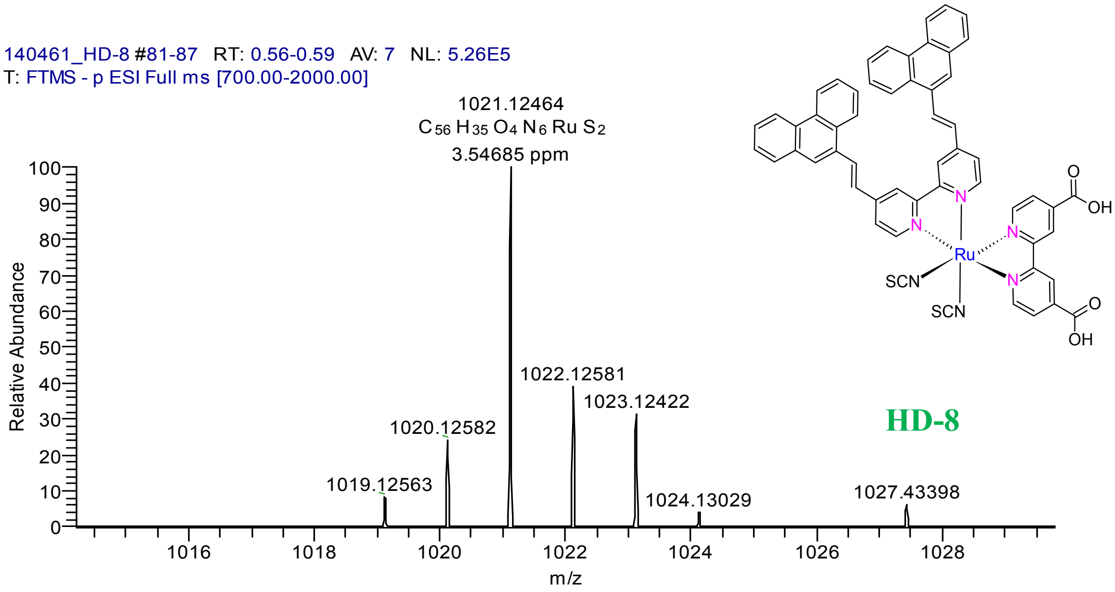


Figure S6. ESI mass spectrum of **HD-8**, $[M - 1H]^{-1}$; Theo. M/Z = 1021.12102, Found. M/Z 1021.12464, Error = 3.547ppm.

3.5. Cyclic Voltammetry Results

Cyclic voltammetry (CV) was used to measure the ground state oxidation potential (GSOP) of LH-7, LH-8, HD-7 and HD-8 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. Fc/Fc^+ was used as internal standard and converted to NHE by addition of 0.63 V. Figures S7 and S8 show the CV graphs of HD-7, and HD-8, respectively. CV graphs were used to calculate the oxidation onset which is equivalent to the GSOP (ground state oxidation potential) or HOMO level. The values of E_{0-0} and GSOP were used to calculate the ESOP (excited state oxidation potential) the values in volts (V) against NHE were converted to electron volt (eV) according to Equation 1[4].

$$\text{ESOP} = [(\text{GSOP (V)} + 4.7) - E_{0-0}]\ \text{eV} \qquad \text{Equation (1)}$$

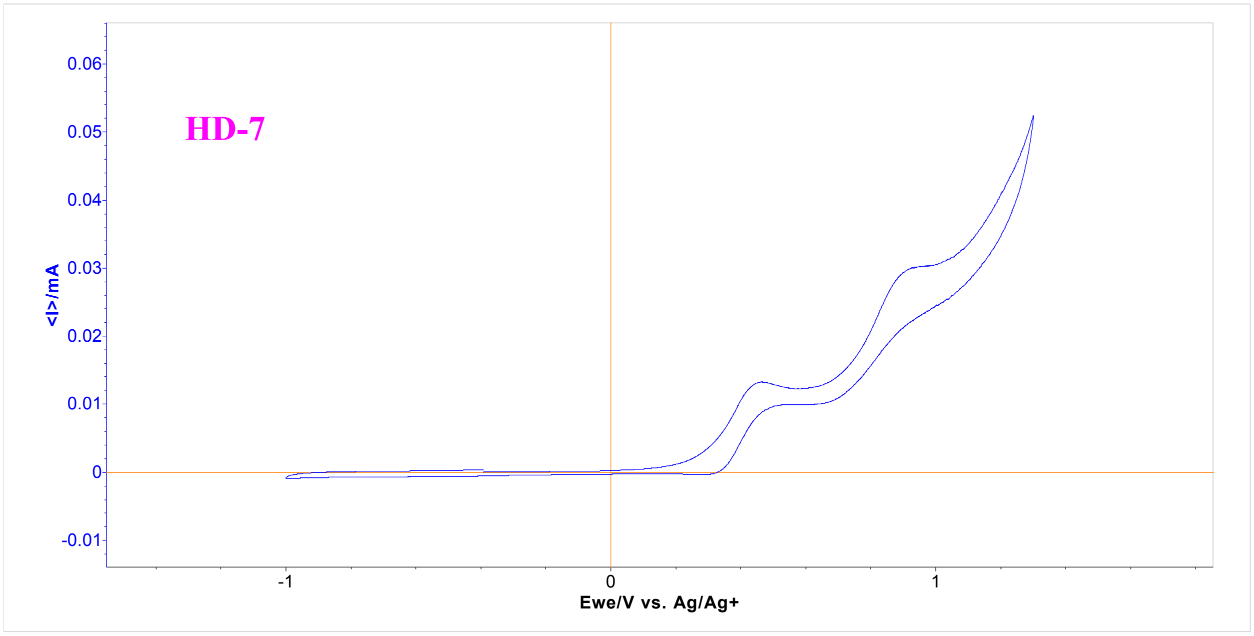


Figure S7. CV graph of HD-7 (-5.46eV)

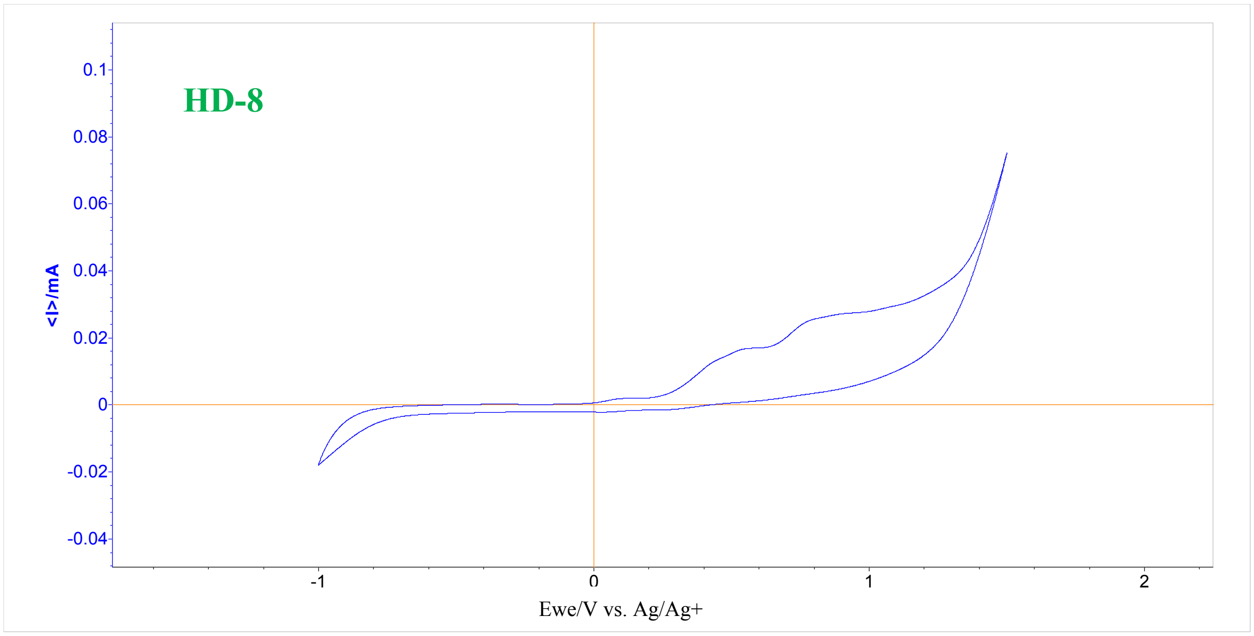


Figure S8. CV graph of HD-8 (-5.45eV)

Table S2. ESOP, GSOP and E_{0-0} for ancillary ligands and sensitizers

Sensitizer	Experimental (eV)		
	*E_{0-0}	♥GSOP(HOMO)	E* (ESOP)
LH-7	2.81	-5.58	-2.77
LH-8	3.06	-5.74	-2.66
HD-7	1.86	-5.46	-3.6
HD-8	1.91	-5.45	-3.54
N719	1.99	-5.76	-3.77

♥GSOP=ground state oxidation potential= E_{HOMO}; *E_{0-0}= calculated from the onset of absorption (DMF), ♥ GSOP was measured in DMF with 0.1 M [TBA][PF_6] and with a scan rate of 50 mV s^{-1}. It was calibrated with Fc/Fc^+ as internal reference and converted to NHE by addition of 0.63 V. Excited-state oxidation potential, E*, was calculated from: E* = GSOP - *E_{0-0}. Calculated GSOP, ESOP, and E_{0-0} of N719 was performed elsewhere [5].

3.6. TiO_2 Electrode Preparation

The photo-anodes composed of nanocrystalline TiO_2 and counter electrode were prepared using literature procedures [6]. Fluorine-doped tin oxide (FTO) coated glasses (2.2 mm thickness, sheet resistance of 8 Ω/cm^2, TEC, Pilkington) were washed with detergent, water, acetone and ethanol, sequentially. After this FTO glass plates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. Thin layer of TiO_2 (10-12µm) (Solaronix, Ti-Nanoxide D/SP) was deposited (active area, 0.18 cm^2) on transparent conducting glass by squeegee printing. After drying the electrodes at 120 °C for 6 min, scattering layer of larger TiO_2 particles (5 µm thick) (Solaronix, Ti-Nanoxide R/SP) were printed. The TiO_2 electrodes were heated under an air flow at 350 °C for 10 min, followed by heating at 500 °C for 30 min. After cooling to room temperature, the TiO_2 electrodes were treated with 40 mM aqueous solution of $TiCl_4$ at 70 °C for 30 min and then washed with water and ethanol. The electrodes were heated again at 500 °C for 30 min and left to cool to 80 °C before dipping them into the dye solution. The dye solutions (0.3 mM) 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.

For preparing counter electrode pre-cut TCO glasses were washed with water H_2O followed by 0.1M HCl in EtOH wash and sonication in acetone bath for 10min. These washed TCO were then dried at 400 °C for 15min. Thin layer of Pt-paste (Solaronix, Platisol T/SP) on TCO was printed and the printed electrodes were then cured at 450 °C for 10 mints.

The dye sensitized TiO_2 electrodes were sandwiched with Pt counter electrodes and the electrolyte (Solaronix, Iodolyte AN-50) was then injected into the cell, while the two electrodes were held together with the clips.

3.7. Fabrication of Dye-Sensitized Solar Cell.

Photocurrent-voltage characteristics of DSCs were measured using a Keithley 2400 source meter under illumination of AM 1.5 G solar light from solar simulator (SOL3A, Oriel) equipped with a 450 W xenon lamp (91160, Oriel). The incident light intensity was calibrated using a reference Si solar cell (Newport Oriel, 91150V) to set 1 Sun (100 mW/cm^2). The measurement was fully controlled under Oriel IV Test Station software.

3.8. Incident Photon to Current Efficiency (IPCE) Conversion

IPCE (incident monochromatic photon to current conversion efficiency) experiments were carried out using a system (QEX10, PV Measurements, USA) equipped with a 75 W short arc xenon lamp (UXL-75XE, USHIO, Japan) as a light source connected to a monochrometer. Calibration of incident light was performed before measurements using a silicone photodiode (IF035, PV Measuremnts). All the measurements were carried out without the use of anti-reflecting film.

3.9. Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectra were measured with an impedance analyzer in 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, and the AC amplitude was set at 10mV. The electrical impedance spectra were fitted using Z-Fit software (Bio-Logic).

3.10. 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 dye films which were used for TAS and TCSPC studies were prepared by first squeeze printing the transparent TiO_2 nanoparticles (active area 0.18cm^2) on clean glass slides followed by annealing at 500C for 30hr. These electrodes were then dipped in dye solution (2*10^{-4}M, solvent 1:1:1 acetonitrile, tert-butyl alcohol and DMSO) facing up for two hours at room temperature without any additives in the dye solution. After two hours these electrodes were taken out of the dye solution, rinsed with ethanol, dried and sandwiched with microscope slides covering the active area. Electrolyte was later introduced between the two interfaces.

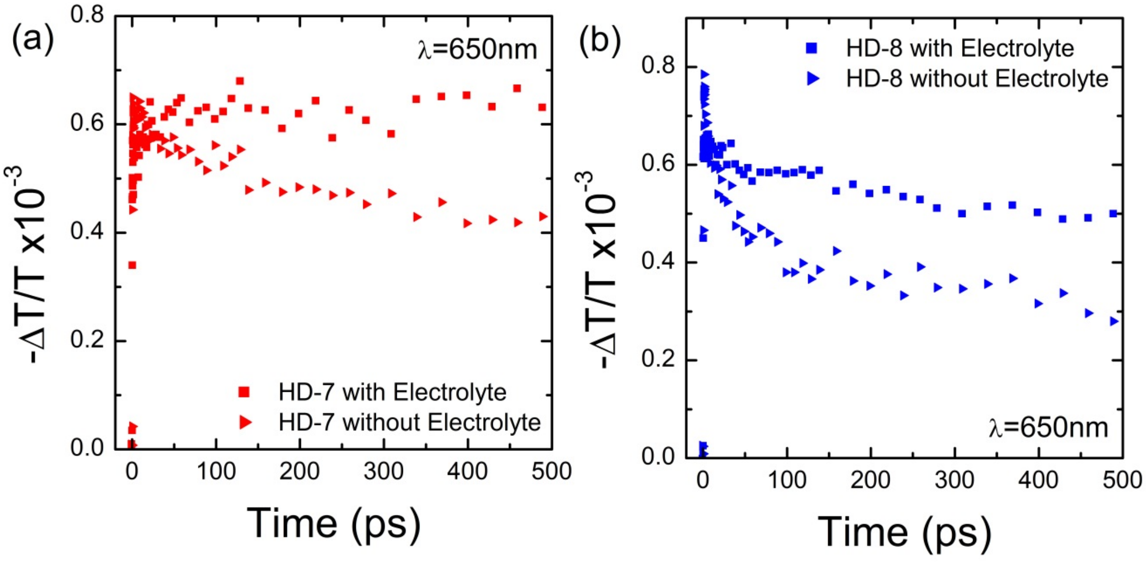


Figure S9. Time evolution of TA spectra of the excited-state dye (dye*) at 650 nm for (a) HD-7 film with and without the electrolyte solution and (b) HD-8 film with and without the electrolyte solution.

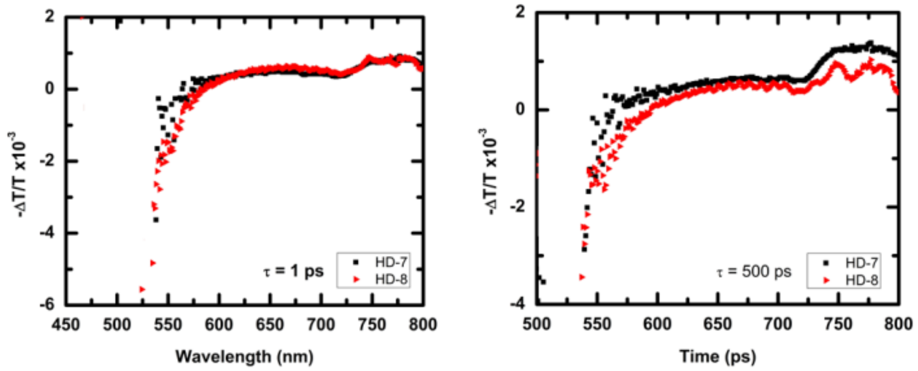


Figure S10. Transient Absorption spectra comparison between HD-7 and HD-8 after (a) 1 ps (b) 500ps with the addition of the iodide-based electrolyte, samples were excited at 530nm.

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