Sequential Series Multijunction Dye-Sensitized Solar Cells (SSM-DSCs): 4.7 Volts from a Single Illuminated Area

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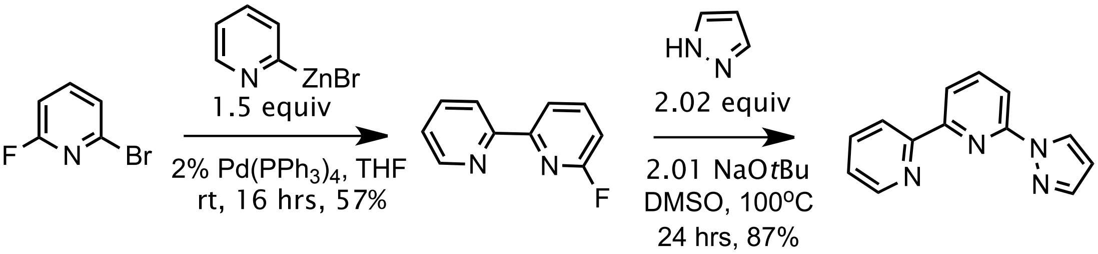
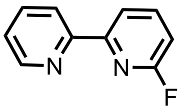
General Information: All commercially obtained reagents and extra dry solvents were used as received. **D35** and **Y123** were purchased from Dyenamo, Sweden. ^{1}H NMR spectra were recorded on a Bruker Avance-500 (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm). Data reported as s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad, ap = apparent, dd = doublet of doublets, and coupling constant(s) are in Hz.

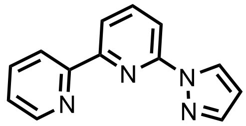
Scheme 1. Modified Synthesis of the bpy-pz ligand for the Co(bpy-pz)$_2^{+2/+3}$ complexes.



The synthesis of Co(bpy-pz)$_2^{+2/+3}$ is known in literature and referenced below. A modified route was used as described below to make the ligand compared to that previously reported. Characterization data matches that of the known compounds.



6-fluoro-2,2'-bipyridine: To an oven dried, N_2 filled round bottom flask was added 17 ml of a 0.5 M solution of pyridin-2-ylzinc (II) bromide (8.50 mmol) in THF and 2-bromo-6-fluoropyridine (1.0 g, 5.67 mmol). Then $Pd(PPh_3)_4$ (0.131 g, 0.11 mmol) was added as a single portion at room temperature. The reaction mixture was stirred at room temperature overnight. The reaction was monitored by TLC until the starting bromo-pyridine had been consumed. The crude product was poured into an EDTA/K_2CO_3 aqueous solution (~100 mL saturated in both EDTA and K_2CO_3) and extracted with Et_2O (~100 mL). The organic layer was separated and dried with Na_2SO_4. After concentration, the product was purified by silica gel (125 mL SiO_2) chromatography with a gradient elution starting with 10% and progressing to 20% ethyl acetate/hexanes to give a white solid (563 mg, 3.23 mmol, 57% yield). ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.71 (d, *J* = 4.7 Hz, 1H), 8.32 (dd, *J* = 7.4, 2.7 Hz, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 8.15 (ap q, *J* = 7.7 Hz, 1H), 7.96 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.50 (dd, *J* = 7.2, 4.7 Hz, 1H), 7.21 (dd, *J* = 8.1, 2.8 Hz, 1H). This molecule was previously prepared through an alternate procedure and the characterization data was in agreement.[1]



6-(1H-pyrazol-1-yl)-2,2'-bipyridine: To an oven dried, N_2 filled round bottom flask was added 1H-pyrazole (479 mg, 7.04 mmol), sodium *tert*-butoxide (678 mg, 7.06 mmol), and 5 ml of N_2-degassed, dry DMSO at room temperature. Note: reaction gives off heat. After stirring for 10 minutes the reaction ceased to give off heated. 6-fluoro-2,2'-bipyridine (1.2 g, 6.89 mmol) was added in one portion. The reaction was heated to 100°C with stirring and monitored by TLC. After 24 hours, the reaction was cooled to room temperature and the mixture was extracted with Et_2O (~100 mL) and H_2O (~100 mL). The organics were separated and dried with Na_2SO_4. The concentrated mixture was then purified by silica gel chromatography first by eluting 100% DCM to remove any excess pyrazole, then 50% MeOH/DCM to give a white solid (1.3 g, 5.99 mmol, 87% yield). ^{1}H NMR (300 MHz, d_6-DMSO) δ 8.92 (d, *J* = 1.8 Hz, 1H), 8.72 (d, *J* = 3.8 Hz, 1H), 8.58 (dd, *J* = 7.7, 0.8 Hz, 1H) 8.33 (d, *J* = 7.7 Hz, 1H), 8.11 (t, *J* = 7.7 Hz, 1H), 8.05-7.95 (m, 2H), 7.87 (d, *J* = 0.7 Hz, 1H), 7.51 (dd, *J* = 7.7 ,4.8 Hz, 1H), 6.64 (ap t, *J* = 1.6 Hz, 1H). This molecule was previously prepared through an alternate procedure and the characterization data was in agreement.[1]

Further complexation and oxidation steps were done following literature procedures. $Co(bpy)_3^{2+/3+}$ was prepared by following the literature procedure.[2, 3]

Photovoltaic Characterization

Photovoltaic characteristics were measured using a 150 W xenon lamp (Model SF300A, SCIENCETECH Inc. Class AAA) solar simulator equipped with an AM 1.5 G filter for a less than 2% spectral mismatch. Prior to each measurement, the solar simulator output was calibrated with a KG5 filtered mono-crystalline silicon NREL calibrated reference cell from ABET Technologies (Model 15150-KG5). The current density-voltage characteristic of each cell was obtained with Keithley digital source meter (Model 2400). The incident photon-to-current conversion efficiency was measured with an IPCE instrument manufactured by Dyenamo comprised of a 175 W xenon lamp (CERMAX, Model LX175F), monochromator (Spectral Products, Model CM110, Czerny-Turner, dual-grating), filter wheel (Spectral Products, Model AB301T, fitted with filter AB3044 [440 nm high pass] and filter AB3051 [510 nm high pass]), a calibrated UV-enhanced silicon photodiode reference and Dyenamo issued software.

Electron lifetime measurements, also known as small modulation photovoltage transient measurements, were carried out with a Dyenamo Toolbox (DN-AE01) instrument and software. The intensity of the LED light source (Seoul Semiconductors, Natural White, S42182H, 450 nm to 750 nm emission) is varied to modulate the device open-circuit voltage. The base light intensity was modulated by applied voltages of 2.80, 2.85, 2.90, 2.95 and 3.00 V applied to the LED with the 3.0 V bias approaching 1 sun intensity (97%). The direction of illumination was from the photoanode to the counter electrode, and the device was positioned 5 cm from the LED light source. The voltage rise and decay times are fitted with a Levenberg-Marquardt fitting algorithm via LabView, and the electron lifetime was obtained from the averaging of rise and decay times.

Charge extraction at open circuit conditions (Q_{oc}) as function of light intensity was carried out with a Dyenamo Toolbox (DN-AE01) instrument and software. Different open-circuit values were achieved by the programmed control of a biased LED (description above) from 2.5 V to 3.2 V. The LED is switched on for 1 second of illumination, then switched off for 10 seconds with a simultaneous switch to short-circuit conditions and monitoring of current. The total charge is found by integrating the current measured over time.

Device Fabrication

Photoanode preparation: **D35** and **Y123** full devices (with scattering layer) were prepared exactly the same way as is reported previously.[4] TEC 10 FTO glass (10 Ω/sq. sheet resistance: FTO [fluorine doped tin oxide]) for the final subcell in the SSM-DSC devices with scattering layer was used and TEC 15 FTO glass (15 Ω/sq. sheet resistance: FTO) for all other subcells for both photoanode and cathode was used and was purchased from Hartford Glass. Once cut into 2x2 cm squares the substrate was submerged in a 0.2% Deconex 21 aqueous solution and sonicated for 15 minutes at room temperature. The electrodes were rinsed with water, sonicated in acetone 10 minutes, and sonicated in ethanol for 10 minutes. The electrodes were then placed under UV/ozone for 15 minutes (UV-Ozone Cleaning System, Model ProCleaner by UVFAB Systems). A compact TiO_2 underlayer is then applied by pre-treatment of the substrate submerged in a 40 mM $TiCl_4$ solution in water (prepared by careful water addition to 99.9% $TiCl_4$ at 0-5 ^{O}C). The submerged substrates (conductive side up) were heated for 30 minutes at 70^{o}C. After heating, the substrates were rinsed first with water then with ethanol. A thickness between 1.2 and 4.5 μm mesoporous P30 TiO_2 layer (particle size: 30 nm, Dyenamo, DN-GPS-30TS, >99% anatase) was screen printed from a Sefar screen (54/137–64W) resulting in 4.5 μm or Sefar screen (90/230-48W) resulting in 2.2 μm thickness on average for each print. For thickness of 1.2 μm and 0.8 μm, the commercial P30 paste was diluted with terpineol (2:1, paste:terpineol) and (1:1, paste:terpineol), respectively, and printed with Sefar screen (90/230-48W). For thickness of 1.5 μm, P30 paste was diluted with terpineol (2:1, paste:terpineol) and printed with Sefar screen (54/137–64W). Particle sizes were indicated to be typically within ± 2 nm of the average and are >99% anatase at the time of paste formulation as indicated by the distributor. A 5 μm TiO_2 scattering layer (for full device) (particle size: >100 nm, Solaronix R/SP) was screen printed onto electrodes where indicated. Between each print of TiO_2 paste, the substrate was heated for 7 minutes at 125 ^oC and the thickness was measured with a profilometer (Alpha-Step D-500 KLA Tencor). The substrate was then sintered with progressive heating from 125^oC (5 minute ramp from r.t., 5 minute hold) to 325 ^oC (15 minute ramp from 125^oC, 5 minute hold) to 375 ^oC (5 minute ramp from 325 ^oC, 5 minute hold) to 450 ^oC (5 minute ramp from 375 ^oC, 15 minute hold) to 500 ^oC (5 minute ramp from 450 ^oC, 15 minute hold) using a programmable furnace (Vulcan® 3-Series model 3-550). All reported device thicknesses were measured post-sintering. The cooled, sintered photoanode was soaked 30 minutes at 70 ^0C in a 40 mM $TiCl_4$ water solution and heated at 40 ^oC per minute to 500^oC and held at 500 ^oC for 30 minutes prior to sensitization. The complete working electrode was prepared by immersing the TiO_2 film into a **D35** dye solution (0.3 mM, 4:1 (EtOH:THF)), with 40x (12 mM) of chenodeoxycholic acid (CDCA), or **Y123** dye solution (0.2 mM, 1:1 (ACN:*tert*-butanol)) with 50x CDCA.[5] The electrodes were immersed in these dye solutions at room temperature for 6 hours.

Counter Electrode Preparation: Two holes were drilled through the insulating side to the conductive side of 2 x 2 cm squares of TEC 7 FTO glass (7 Ω/sq. sheet resistance) for full subcells, and TEC 15 FTO glass (15 Ω/sq. sheet resistance) for all other subcells, using a Dremel-4000 with a Dremel 7134 Diamond Taper Point Bit submerged in water to reduce glass cracking with Scotch tape on the FTO side to minimize scratching. The tape was removed, and the electrodes were washed with water followed by a 0.1 M HCl in EtOH solution. The electrodes were then sonicated in an acetone bath for 10 minutes and dried at 400 °C for 15 minutes. For platinum electrodes: A thin layer of Pt-paste (Solaronix, Platisol T/SP) was slot printed with a punched Scotch tape piece on the conductive side. The electrodes were then heated at 450°C for 10 minutes.

PEDOT electrodes: PEDOT electrodes were prepared following the previously reported procedure.[6] Briefly, an aqueous solution of 0.1 M sodium dodecylsulfate (SDS, Biotechnology Grade, VWR) and 0.01 M 3,4-ethylenedioxythiophene (EDOT, 97%, Alfa Aesar) was prepared through sonicating for 90 minutes. Electro-oxidative polymerization was performed by a CHI 6054E potentiostat. In a two electrode cell, a 2 × 2 cm cleaned, predrilled FTO glass substrate was used as a working electrode and same size cleaned FTO was used as counter and reference electrode. Electro-oxidative polymerization was performed under galvanostatic (chronopotentiometry on the instrument) mode with the following parameters: anodic current valued at 3 mA, high and low potential (E) 3.5-2.5 V, low E hold time 0 seconds, cathodic time of 0.005 seconds, anodic time 70 seconds, with initial polarity anodic, data storage interval as 0.1 seconds and number of segments 2, where current switching priority was based on time. The blue colored films were rinsed thoroughly with deionized water and dried for 2 minutes at 125 ^{o}C before use.

Dye-sensitized Solar Cell assembly: The photoanode and counter electrode were sealed with a 25 μm thick hot melt gasket (Surlyn, Solaronix, "Meltonix 1170-25") by heating the system at 130 °C under a pressure of 0.2 psi for 1 minute with a sealing machine (Dyenamo, product DN-HM01). The electrolyte was added through the pre-drilled holes in the counter electrodes with the rubber sealing tip from a Solaronix "Vac'n'Fill Syringe" until the electrolyte began to emerge from the second counter electrode hole. The holes were sealed with a Surlyn sheet and a thin glass cover by heating at 130 °C under pressure (0.1 psi) for 25 seconds both for full and thin devices. Finally, soldered contacts were added with a MBR Ultrasonic soldering machine (model USS-9210) with solder alloy (Cerasolzer wire diameter 1.6 mm, item # CS186-150). A circular black mask (active area 0.15 cm^2) punched from black tape was used in the subsequent photovoltaic studies.

Photoanode Surface Treatment

PFTS treatment: Sensitized TiO_2 films were submerged in a 0.1 M solution of 97% 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (PFTS) in hexanes for 90 minutes at 30 ^{o}C. The electrodes were rinsed with hexanes and assembled as described above.

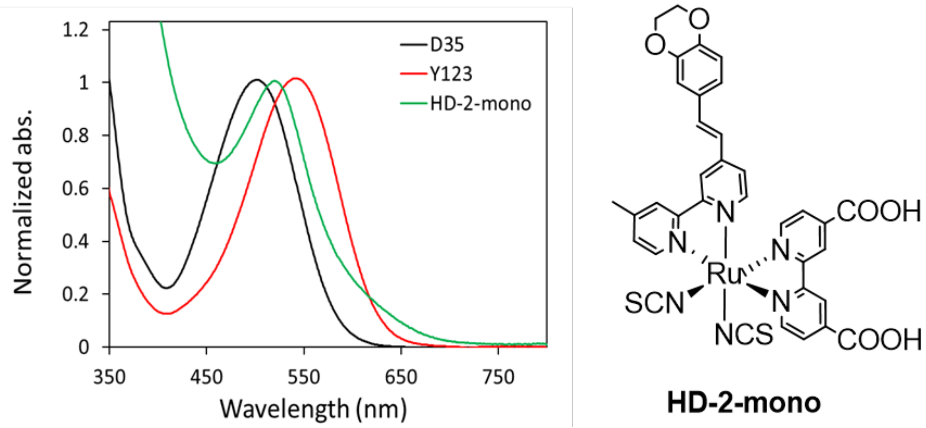


Figure S1. UV-Vis absorption profile of **D35** and **Y123** in DCM with **HD-2-mono** in DMF.

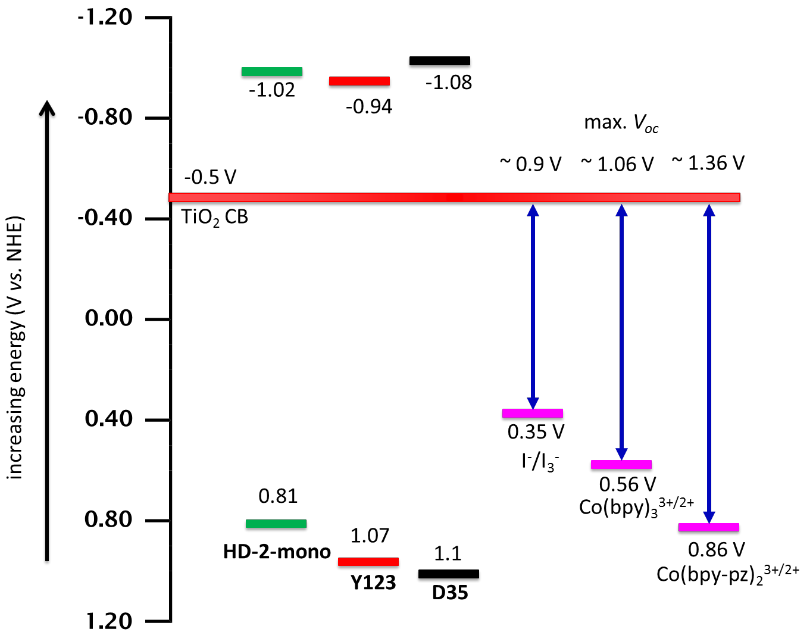


Figure S2. D35, **Y123** and **HD-2-mono** energetics and theoretical maximum possible values when paired with I^-/I_3^-, $Co(bpy)_3^{+2/+3}$ and $Co(bpy\text{-}pz)_2^{+2/+3}$. **D35** was measured on TiO_2.[7] **Y123** energetics are reported previously.[7] **HD-2-mono** was measured in DMF solution. Redox shuttle values are measured in MeCN.

Table S1. SSM-DSC results for 2-5 subcell systems with **D35**, **Y123** and **HD-2-mono**.

entry #	subcell type	thickness (μm)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE %
1	**D35/D35**	1.5/full	1965±5	4.9±0.1	0.71±0.01	6.9±0.2
2	**D35/Y123**	1.5/full	1918±19	5.9±0.2	0.62±0.01	7.1±0.2
3	**D35/D35/Y123**	1.2/2.2/full	2871±14	3.9±0.2	0.55±0.04	6.4±0.1
4	**D35/Y123/Y123**	1.2/2.2/full	2809±8	3.7±0.1	0.61±0.01	6.4±0.1
5	**D35/Y123/Y123**[a]	1.2/2.2/full	2666±5	3.6±0.2	0.72±0.02	7.0±0.02
6	**D35/Y123/HD-2-mono**	1.2/2.2/full	2628±17	3.9±0.3	0.74±0.03	7.7±0.1
7	**D35/D35/Y123/ Y123**	0.8/2.2/2.2/ full	3718±8	2.7±0.1	0.58±0.03	5.8±0.2
8	**D35/D35/Y123/ Y123/Y123**	0.8/2.2/1.2/ 2.2/full	4670±38	2.4±0.1	0.38±0.05	4.3±0.3
9	**D35/D35/Y123/ Y123/HD-2-mono**	0.8/2.2/1.2/ 2.2/full	4377±12	2.9±0.5	0.35±0.02	4.4±0.3
10	4+4 (Table S5, entry 4)		7516	1.7	0.34	4.4
11	4+5 (Table S5, entry 4 & 6)		8546	1.9	0.25	4.1

Front cells are the first dyes listed with the respective thickness of the TiO_2 film listed first as well. Subsequent subcells are listed in order from front to back. "Full" indicates subcells use a 4.5 μm TiO_2 active layer and a 4.5 μm TiO_2 scattering layer. Electrolyte used for all cells unless otherwise noted is as follows: 0.25 M Co(bpy-pz)$_2$(PF$_6$)$_2$, 0.05 M Co(bpy-pz)$_2$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile. [a]Indicates Co(bpy)$_3^{3+/2+}$ was used in this subcell. Device parameters are the average of 3 SSM-DSC cells.

Table S2. Optical and electrochemical properties of **D35**, **Y123** and **HD-2-mono**.

Dye	λ_{onset} (nm)[a]	λ_{max} (nm)[a]	ε (M^{-1}cm^{-1})[a]	$E_{(S+/S)}$ (V vs NHE)[b]	$E_{(S+/S*)}$ (V vs NHE)[c]	E_g^{opt} (eV)[d]
D35	570	500	31000	1.10	-1.08	2.18
Y123	650	540	49000	1.07	-0.94	2.01
HD-2-mono	680	539	13900	0.81	-1.02	1.83

[a]**D35** was measured in DCM.[8] **Y123** was also measured in DCM.[9] **HD-2-mono** was measured in DMF.[10] λ_{onset} was estimated by drawing a tangent line on the low energy side of the lowest enery transition and reporting the value as the intersection of the x-axis. [b]**D35 and Y123** were measured on TiO_2.[7] **HD-2-mono** was measured in DMF with glassy carbon working electrode, platinum wire as counter electrode and Ag/AgNO$_3$ as the reference electrode. Ferrocene was used an an internal reference to calibrate the reference electrode. Ferrocene was taken as 0.63 V vs NHE in DMF. [c]$E_{(S+/S*)} = E_{(S+/S)} - E_g^{opt}$. [d] E_g^{opt} was calculated from the equation $E_g^{opt} = 1240\ (nm)(eV)/\ \lambda_{onset}$.

Table S3. **D35** and **Y123** optimizations with Co(bpy-pz)$_2^{3+/2+}$ electrolyte and FSAM surface treatment.

entry #	dye and TiO$_2$ thickness	treatment	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE %
Co(bpy-pz)$_2^{3+/2+}$ electrolyte and surface treatment optimization with a scattering layer						
1	**D35** full	None[a]	953±3	7.1±0.3	74±1	5.1±0.3
2		None	998±7	7.9±0.2	72±4	5.9±0.4
3		FSAM	1037±15	8.7±0.4	74±2	6.8±0.08
4	**Y123** full	None	965±0	9.7±0.3	67±0.2	6.6±0.2
5		None[b]	959±21	11.4±0.3	72±2	8.1±0.3
6		FSAM[b]	946±5	9.6±0.3	71±0.9	6.5±0.3
Co(bpy-pz)$_2^{3+/2+}$ devices with thin TiO$_2$ films, without a scattering layer						
7	**D35** 0.8 µm	FSAM	981±7	2.8±0.1	70±3	2±0.2
8	**D35** 1.2 µm	FSAM	979±17	3.7±0.1	69±0.5	2.5±0.1
9	**D35** 1.5 µm	FSAM	997±9	5.1±0.2	69±2	3.5±0.1
10	**D35** 2.2 µm	FSAM	1031±8	7.1±0.5	68±2	5.4±0.4
11	**Y123** 1.2 µm	None	1010±2	5.2±0.1	64±1.4	3.5±0.2
12	**Y123** 2.2 µm	None	1010±2	7.5±0.05	70±1.7	5.4±0.08

All cells employ an optimized electrolyte having concentrations as: 0.25 M Co(bpy-pz)$_2$(PF$_6$)$_2$, 0.05 M Co(bpy-pz)$_2$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile unless otherwise noted. Devices employ a Pt counter electrode unless otherwise noted. Device parameters are the average of 3 cells. Active area was fixed at 0.15 cm^2 throughout the study, with a black tape mask. Values after cell type refer to TiO$_2$ film thickness. "full" refers to a 4.5 µm active layer of 30 nm particles and a 4.5 µm scattering layer. [a]Electrolyte with concentrations as previously reported for **Y123**, which was comprised of: 0.22 M Co(bpy-pz)$_2$(PF$_6$)$_2$, 0.05 M Co(bpy-pz)$_2$(PF$_6$)$_3$, 0.1 M LiClO$_4$, and 0.2 M *tert*-butylpyridine, in acetonitrile.[5] [b]PEDOT counter electrode used.

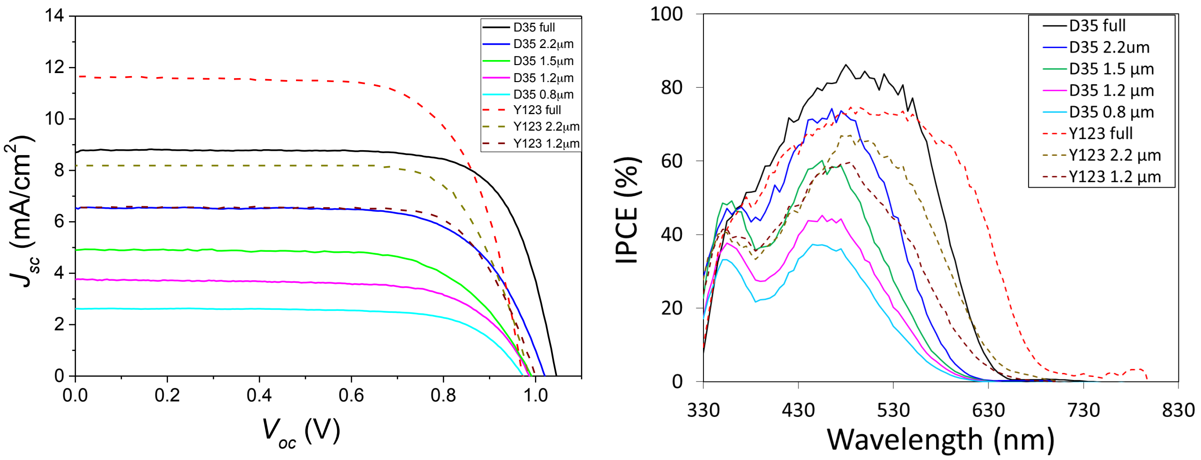


Figure S3. IV curves (left) and IPCE (right) of optimized Co(bpy-pz)$_2^{3+/2+}$ based devices in Table S3 for **D35** (solid lines) and **Y123** (dotted lines).

Table S4. **D35**, **Y123** and **HD-2-mono** optimization with Co(bpy)$_3^{3+/2+}$ electrolyte and FSAM surface treatment.

entry #	dye and TiO$_2$ thickness	treatment	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE %
Co(bpy)$_3^{3+/2+}$ electrolyte and surface treatment optimization with scattering layer						
1	**D35**^{a,b}	None	854±6	10.3±0.3	73±1.8	6.6±0.1
2	**D35**^{b}	None	854±14	10.7±0.5	74±1	6.9±0.2
3		FSAM	921±15	10.2±0.6	73±4	7±0.4
4	**Y123**^{b}	none	842±23	12.3±1.3	72±1	7.7±0.4
5	**HD-2-mono**^{c,d}	none	719 ± 8	16.6 ± 0.1	73 ± 0.01	8.8 ± 0.1
Co(bpy)$_3^{3+/2+}$ devices with different thickness and without scattering layer						
6	**D35** 1.2 μm	FSAM	993±23	3.2±0.15	73±1.4	2.4±0.08
7	**D35** 2.2 μm	FSAM	974±14	6.1±0.4	67±3	4.1±0.2
8	**Y123** 1.2 μm	None	973±28	5.5±0.3	66±8	3.6±0.3
9	**Y123** 2.2 μm	None	898±25	7.4±0.96	70±4	5±0.5

All cells employ the optimized electrolyte having concentrations as: 0.25 M Co(bpy)$_3$(PF$_6$)$_2$, 0.05 M Co (bpy)$_3$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine in acetonitrile unless otherwise noted. [a]Electrolyte with concentrations as: 0.25 M Co (bpy)$_3$(PF$_6$)$_2$, 0.05 M Co(bpy)$_3$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.25 M *tert*-butylpyridine in acetonitrile. [b]Electrode thickness was 4.5 μm 30 nm TiO$_2$ particles and 4.5 μm scattering layer. [c]Electrode thickness was 10.0 μm 30 nm TiO$_2$ particles and 4.5 μm scattering layer. [d]Iodine electrolyte was used: 1.0 M DMII (1,3-dimethylimidazolium iodide), 0.05 M LiI, 30 mM I$_2$, 0.5 M TBP (4-*tert*-butylpyridine), 0.1 M GNCS (guanadinium thiocyanate) in acetonitrile and valeronitrile (v/v, 85/15).

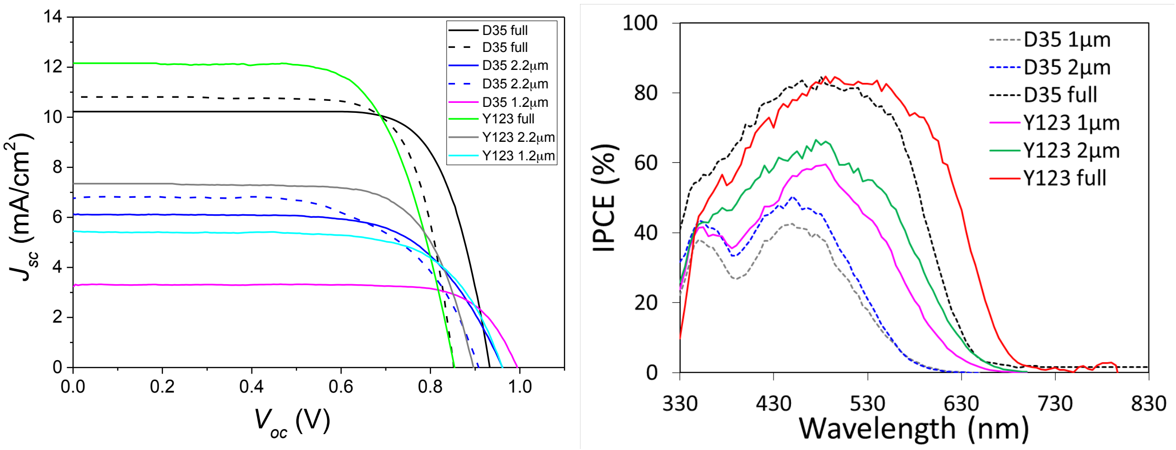


Figure S4. IV (top) and IPCE (bottom) of Co(bpy)$_3^{3+/2+}$ based devices in Table S4.

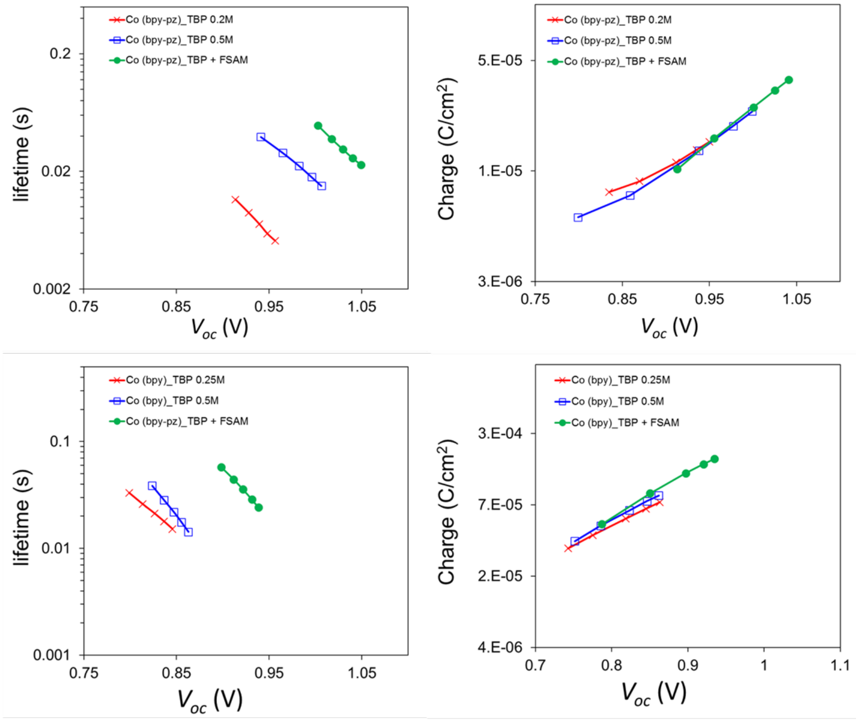


Figure S5. Photovoltage transient measurement plotted as electron lifetime versus open-circuit voltage and charge density versus open-circuit voltage for Co(bpy-pz)$_2^{3+/2+}$ (top) and Co(bpy)$_3^{+3/+2}$ (bottom).

Table S5. SSM-DSC results for comparison of different front cells thicknesses.

entry #	**subcell type**	**thickness (µm)**	**V_{oc} (mV)**	**J_{sc} (mA/cm^2)**	**FF**	**PCE %**
1	**D35/Y123**	1.5/full	1918±19	5.9±0.2	0.62±0.01	7.1±0.2
2	**D35/Y123**	2.2/full	1930±10	7.2±0.2	0.51±0.01	7.2±0.3
3	**D35/D35/Y123/ Y123**	0.8/2.2/2.2/ full	3718±8	2.7±0.1	0.58±0.03	5.8±0.2
4	**D35/D35/Y123/ Y123**	1.2/2.2/2.2/ full	3776±9	4.1±0.3	0.35±0.02	5.4±0.2
5	**D35/D35/Y123/ Y123/Y123**	0.8/2.2/1.2/ 2.2/full	4670±38	2.4±0.1	0.38±0.05	4.3±0.3
6	**D35/D35/Y123/ Y123/Y123**	1.2/2.2/1.2/ 2.2/full	4667±32	3.7±0.1	0.22±0.03	3.8±0.4

Front cells are the first dyes listed with the respective thickness of the TiO_2 film listed first as well. Subsequent subcells are listed in order from front to back. The overall power conversion efficiency (PCE) is calculated through the equation: PCE = (V_{oc} x J_{sc} x FF)/I_o, where V_{oc} is the open circuit voltage, J_{sc} is the short-circuit current density, FF is the fill factor and I_o is the incident light intensity. “Full” indicates subcells use a 4.5 µm TiO_2 active layer and a 4.5 µm TiO_2 scattering layer. Electrolyte used for all cells unless otherwise noted is as follows: 0.25 M $Co(bpy\text{-}pz)_2(PF_6)_2$, 0.05 M $Co(bpy\text{-}pz)_2(PF_6)_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile.

Table S6. Multijunction device and its individual subcell photovoltaic characteristics for $Co(bpy\text{-}pz)_3^{3+/2+}$ based electrolyte with two and three stacked devices.

dye and TiO_2 thickness (µm)	Position	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF %	PCE %
D35/D35					
D35 1.5 µm	itself	997±9	5.1±0.2	69±2	3.5±0.1
D35 full	itself	1037±15	8.7±0.4	74±2	6.8±0.08
	2nd	984±8	4.9±0.1	73±2	4.0±0.2
D35/D35 (1.5/full)	**Multijunction**	**1965±5**	**4.9±0.05**	**71±1**	**6.9±0.2**
D35/Y123					
D35 1.5 µm	itself	997±9	5.1±0.2	69±2	3.5±0.1
Y123 full	itself	959±21	11.4±0.3	72±2	8.1±0.3
	2nd	905±13	6.2±0.4	77±2	4.5±0.4
D35/Y123 (1.5/full)	**Multijunction**	**1918±19**	**5.9±0.2**	**62±1**	**7.1±0.2**
D35/D35/Y123					
D35 1.2 µm	itself	979±17	3.7±0.1	69±0.5	2.5±0.1
D35 2.2 µm	itself	1031±8	7.1±0.5	68±2	5.4±0.4
	2nd	987±5	2.3±0.2	71±5	1.8±0.03
Y123 full	itself	959±21	11.4±0.3	72±2	8.1±0.3
	3rd	876±26	3.3±0.1	78±1	2.4±0.02
D35/D35/Y123 (1.2/2.2/full)	**Multijunction**	**2871±14**	**3.9±0.2**	**55±4**	**6.4±0.1**

“itself” refers to measurements made on this subcell when taken out of the SSM-DSC configuration and measured directly. “2nd or 3rd” refers to measurements made on this specific subcell only, when in the SSM-DSC configuration. Front cells are the first dyes listed with the respective thickness of the TiO_2 film listed first as well. Subsequent subcells are listed in order from front to back. “Full” indicates subcells use a 4.5 µm TiO_2 active layer and a 4.5 µm TiO_2 scattering layer. Electrolyte used for all cells unless otherwise noted is as follows: 0.25 M $Co(bpy\text{-}pz)_2(PF_6)_2$, 0.05 M $Co(bpy\text{-}pz)_2(PF_6)_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile.

Table S7. Multijunction SSM-DSC devices and subcell photovoltaic characteristics for varying electrolyte at the final cell.

dye and TiO$_2$ thickness	Position	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE %
front two subcells based on D35/Y123 used for the remainder of the table					
D35 1.2 μm	itself	979±17	3.7±0.1	69±0.5	2.5±0.1
Y123 2.2 μm	itself	998±12	7.9±0.4	71±2	5.7±0.3
	2nd	958±8	3.7±0.2	76±2	2.7±0.2
3rd (and final) subcell based on Y123 employing Co(bpy-pz)$_2^{3+/2+}$					
Y123 full	itself	959±21	11.4±0.3	72±2	8.1±0.3
	3rd	883±15	2.6±0.05	78±1	1.9±0.05
D35/Y123/Y123	**Multijunction**	**2809±8**	**3.7±0.1**	**61±1**	**6.4±0.1**
3rd (and final) subcell based on Y123 employing Co(bpy)$_3^{3+/2+}$					
Y123 full	itself	811±18	12.3±0.5	73±2	7.6±0.2
	3rd	732±20	3.2±0.1	78±0.6	2.0±0.1
D35/Y123/Y123	**Multijunction**	**2666±5**	**3.6±0.2**	**72±2**	**7.0±0.02**
3rd (and final) subcell based on HD-2-mono employing (I^-/I_3^-)					
HD-2-mono full	itself	719 ± 8	16.6 ± 0.1	0.73 ± 0.01	8.8 ± 0.1
	3rd	688±20	3.6±0.05	78±1	1.84±0.1
D35/Y123/HD-2-mono	**Multijunction**	**2628±17**	**3.9±0.3**	**74±3**	**7.7±0.1**

"itself" refers to measurements made on this subcell when taken out of the SSM-DSC configuration and measured directly. "2nd or 3rd" refers to measurements made on this specific subcell only, when in the SSM-DSC configuration. Front cells are the first dyes listed with the respective thickness of the TiO$_2$ film listed first as well. Subsequent subcells are listed in order from front to back. "Full" indicates subcells use a 4.5 μm TiO$_2$ active layer and a 4.5 μm TiO$_2$ scattering layer. Electrolyte used for all cells unless otherwise noted is as follows: for Co(bpy-pz)$_2^{3+/2+}$: 0.25 M Co(bpy-pz)$_2$(PF$_6$)$_2$, 0.05 M Co(bpy-pz)$_2$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile; for Co(bpy)$_2^{3+/2+}$: 0.25 M Co(bpy-pz)$_2$(PF$_6$)$_2$, 0.05 M Co(bpy-pz)$_2$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile; for I^-/I_3^-: electrode thickness was 10.0 μm 30 nm TiO$_2$ particles and 4.5 μm scattering layer. Iodine electrolyte was used: 1.0 M DMII (1,3- dimethylimidazolium iodide), 0.05 M LiI, 30 mM I$_2$, 0.5 M TBP (4-*tert*-butylpyridine), 0.1 M GNCS (guanadinium thiocyanate) in acetonitrile and valeronitrile (v/v, 85/15).

Table S8. SSM-DSCs and individual subcell photovoltaic characteristics for Co(bpy-pz)$_3^{3+/2+}$ based electrolyte with 4 and 5 stacked devices. See Table S6 for device parameters.

dye and TiO$_2$ thickness	Position	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE %
D35 (0.8 μm)/**D35/Y123/Y123**					
D35 0.8 μm	front	981±7	2.8±0.1	70±3	2±0.2
D35 2.2 μm	itself	1031±8	7.1±0.5	68±2	5.4±0.4
	2nd	970± 22	2.5±0.3	71±02	1.8±0.1
Y123 1.2 μm	itself	998±12	7.9±0.4	71±2	5.7±0.3
	3rd	930±24	2.1±0.3	77±1	1.6±0.3
Y123 full	itself	959±21	11.4±0.3	72±2	8.1±0.3
	4th	887±14	1.9±0.1	78±3	1.4±0.05
D35/D35/Y123/Y123	**Multijunction**	**3718±8**	**2.6±0.1**	**58±3**	**5.8±0.2**
D35 (1.2 μm)/**D35/Y123/Y123**					
D35 1.2 μm	front	979±17	3.7±0.1	69±0.5	2.5±0.1
D35 2.2 μm	itself	1031±8	7.1±0.5	68±2	5.4±0.4
	2nd	987±5	2.3±0.2	71±5	1.8±0.03
Y123 1.2 μm	itself	998±12	7.9±0.4	71±2	5.7±0.3
	3rd	937±5	1.7±0.1	78±1	1.3±0.1
Y123 full	itself	959±21	11.4±0.3	72±2	8.1±0.3
	4th	867±5	1.6±0.05	79±2	1.2±0.02
D35/D35/Y123/Y123	**Multijunction**	**3776±10**	**3.9±0.3**	**35±2**	**5.4±0.2**
D35 (0.8 μm)/**D35/Y123/Y123/Y123**					
D35 0.8 μm	front	981±7	2.8±0.1	70±3	2±0.2
D35 2.2 μm	itself	1031±8	7.1±0.5	68±2	5.4±0.4
	2nd	970± 22	2.5±0.3	71±02	1.8±0.1
Y123 1.2 μm	itself	1003±7	6.3±0.3	71±4	4.6± 0.4
	3rd	941±35	1.3±0.3	75±5	0.94±0.1
Y123 2.2 μm	itself	998±12	7.9±0.4	71±2	5.7±0.3
	4th	925±18	1.1±0.2	74±2	0.75±0.2
Y123 full	itself	959±21	11.4±0.3	72±2	8.1±0.3
	5th	853±10	1.0±0.05	78±2	0.77±0.05
D35/D35/Y123/Y123/Y123	**Multijunction**	**4670±38**	**2.4±0.1**	**38±5**	**4.3±0.3**
D35 (1.2 μm)/**D35/Y123/Y123/Y123**					
D35 1.2 μm	front	979±17	3.7±0.1	69±0.5	2.5±0.1
D35 2.2 μm	itself	1031±8	7.1±0.5	68±2	5.4±0.4
	2nd	987±5	2.3±0.2	71±5	1.8±0.03
Y123 1.2 μm	itself	1003±7	6.3±0.3	71±4	4.6± 0.4
	3rd	927±25	1.0±0.1	79±0.4	0.8±0.1
Y123 2.2 μm	itself	998±12	7.9±0.4	71±2	5.7±0.3
	4th	914±3	0.9±0.08	73±2	0.6±0.02
Y123 full	itself	959±21	11.4±0.3	72±2	8.1±0.3
	5th	852±10	0.9±0.2	79±2	0.7±0.1
D35/D35/Y123/Y123/Y123	**Multijunction**	**4660±32**	**3.7±0.1**	**22±3**	**3.8±0.4**

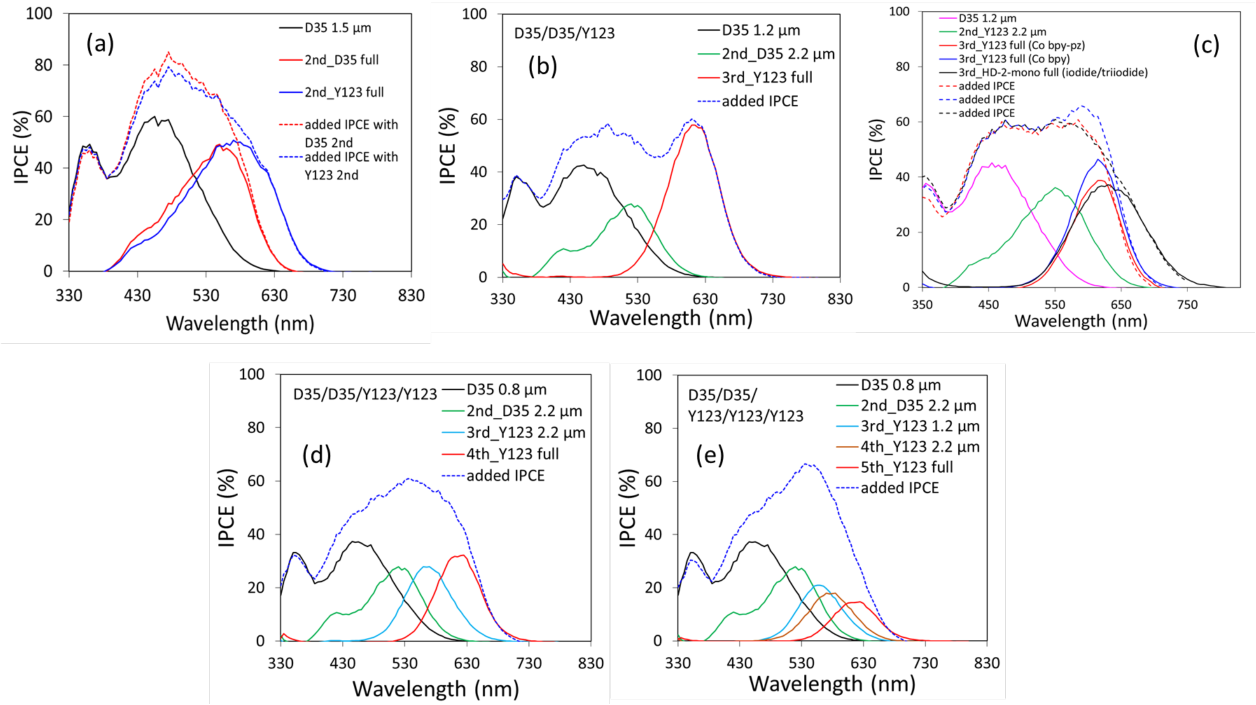


Figure S6. IPCE graphs for individual subcells in the SSM-DSC configuration for Co(bpy-pz)$_2^{3+/2+}$ electrolyte in Table S6-S8. Blue colored dotted line in each graph represent the curve as the result of manual addition of all the IPCE's from devices in the stack.

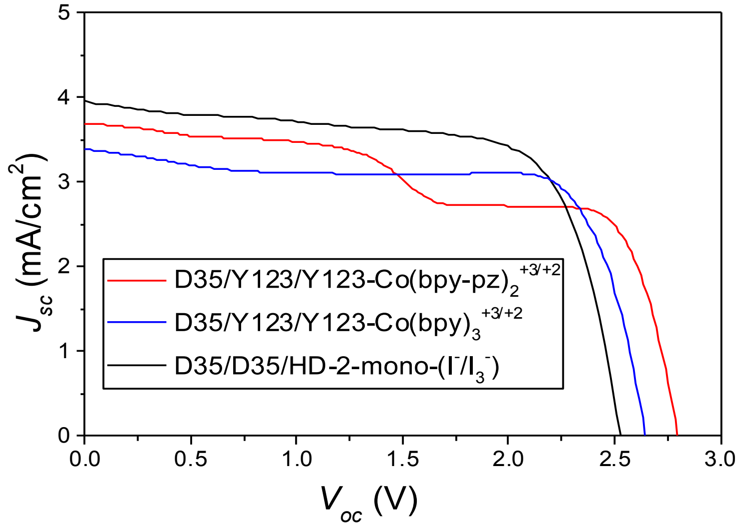


Figure S7. JV curve corresponding to devices reported in Table S7 comparing varying only the third device.

Table S9: Summary of Co(bpy)$_3^{3+/2+}$ based SSM-DSCs.

entry #	dye	thickness (µm)	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF %	PCE %
1	**D35/D35**	1.5/full	1824±5	5.1±0.1	71±1	6.5±0.1
2	**D35/Y123**	2.2/full	1832±12	5.6±0.2	75±3	7.6±0.01
3	**D35/D35/Y123**	1.2/2.2/full	2708±53	3.0±0.7	62±12	4.9±0.1
4	**D35/Y123/Y123**	2.2/2.2/full	2584±30	3.4±0.3	75±5	6.7±0.2
5	**D35/D35/Y123/Y123**	1.2/2.2/2.2/full	3557±54	2.2±0.2	64±8	5.1±0.6
6	**D35/D35/Y123/Y123/ Y123**	1.2/2.2/1.2/2.2/ full	4382±54	2.1±0.3	50±9	4.7±0.3

Front cells are the first dyes listed with the respective thickness of the TiO_2 film listed first as well. Subsequent subcells are listed in order from front to back. “Full” indicates subcells use a 4.5 µm TiO_2 active layer and a 4.5 µm TiO_2 scattering layer. Electrolyte used for all cells unless otherwise noted is as follows: 0.25 M Co(bpy)$_3$(PF$_6$)$_2$, 0.05 M Co(bpy)$_3$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile. Device parameters are the average of 4 SSM-DSC cells.

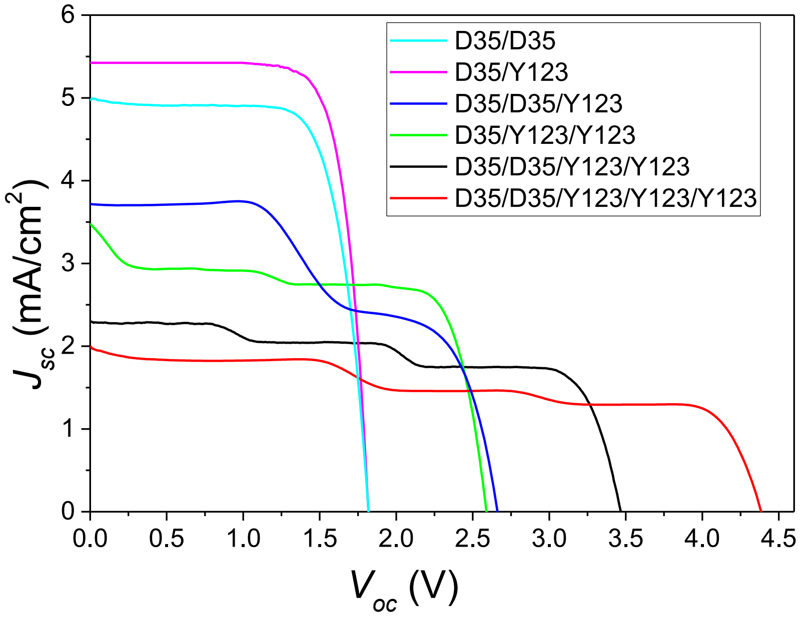


Figure S8. IV results for SSM-DSC devices given in Table S9 for Co(bpy)$_3^{3+/2+}$ electrolyte based devices.

Table S10. Multijunction device and its individual subcell photovoltaic characteristics for Co(bpy)$_3^{3+/2+}$ based electrolyte with 2 to 5 subcell SSM-DSC devices.

dye and TiO$_2$ thickness	position	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF %	PCE %
D35/D35					
D35 2.2 µm	itself	974±14	6.1±0.4	67±3	4.1±0.2
D35 full	itself	921±15	10.2±0.6	73±4	7±0.4
	2nd	885±16	3.8±0.08	79±1	2.7±0.06
D35/D35	**Multijunction**	**1861±19**	**4.7±0.6**	**67±8**	**6±0.1**
D35/Y123					
D35 2.2 µm	itself	974±14	6.1±0.4	67±3	4.1±0.2
Y123 full	itself	842±23	12.3±1.3	72±1	7.7±0.4
	2nd	835±33	5.6±0.05	76±2	3.5±0.1
D35/Y123	**Multijunction**	**1832±12**	**5.6±0.2**	**75±3**	**7.6±0.01**
D35/D35/Y123					
D35 1.2 µm	itself	987±11	3.9±0.1	69±1	2.9±0.03
D35 2.2 µm	itself	948±2	7±0.4	73±1	4.9±0.2
	2nd	930±9	2.4±0.3	71±5	1.7±0.1
Y123 full	itself	837±23	11.9±0.7	73±2	7.6±0.1
	3rd	732±2	3.9±0.1	76±0.5	2.4±0.02
D35/D35/Y123	**Multijunction**	**2666±30**	**3.9±0.1**	**52±1**	**5.3±0.1**
D35/Y123/Y123					
D35 2.2 µm	itself	974±14	6.1±0.4	67±3	4.1±0.2
Y123 2.2 µm	itself	898±25	7.4±0.96	70±4	5±0.5
	2nd	875±5	3.1±0.4	77±4	2.2±0.2
Y123 full	itself	842±23	12.3±1.3	72±1	7.7±0.4
	3rd	732±20	3.4±0.1	78±0.6	2.1±0.1
D35/Y123/Y123	**Multijunction**	**2584±30**	**3.4±0.3**	**75±5**	**6.7±0.2**
D35/D35/Y123/Y123					
D35 1.2 µm	front	993±23	3.2±0.15	73±1.4	2.4±0.08
D35 2.2 µm	itself	974±14	6.1±0.4	67±3	4.1±0.2
	2nd	949±38	2±0.2	77±3	1.3±0.2
Y123 1.2 µm	itself	898±25	7.4±0.96	70±4	5±0.5
	3rd	850±16	1.8±0.4	77±5	1.2±0.2
Y123 full	itself	842±23	12.3±1.3	72±1	7.7±0.4
	4th	762±36	2.6±0.5	79±3	1.6±0.3
D35/D35/Y123/Y123	**Multijunction**	**3557±54**	**2.2±0.2**	**64±8**	**5.1±0.6**
D35/D35/Y123/Y123/Y123					
D35 1.2 µm	front	993±23	3.2±0.15	73±1.4	2.4±0.08
D35 2.2 µm	itself	974±14	6.1±0.4	67±3	4.1±0.2
	2nd	949±38	2±0.2	77±3	1.3±0.2
Y123 1.2 µm	itself	973±28	5.5±0.3	66±8	3.6±0.3
	3rd	910±26	1.3±0.2	78±3	1±0.1
Y123 2.2 µm	itself	898±25	7.4±0.96	70±4	5±0.5
	4th	825±13	1.2±0.08	78±3	0.8±0.04
Y123 full	itself	842±23	12.3±1.3	72±1	7.7±0.4
	5th	747±43	2.1±0.2	78±1	1.4±0.1
D35/D35/Y123/Y123/Y123	**Multijunction**	**4382±54**	**2.1±0.3**	**50±9**	**4.7±0.3**

"itself" refers to measurements made on this subcell when taken out of the SSM-DSC configuration and measured directly. "2nd, 3rd, 4th or 5th" refers to measurements made on this specific subcell only, when in the SSM-DSC configuration. Front cells are the first dyes listed with the respective thickness of the TiO$_2$ film listed first as well. Subsequent subcells are listed in order from front to back. "Full" indicates subcells use a 4.5 µm TiO$_2$ active layer and a 4.5 µm TiO$_2$ scattering layer. Electrolyte used for all cells unless otherwise noted is as follows: 0.25 M Co(bpy)$_2$(PF$_6$)$_2$, 0.05 M Co(bpy)$_2$(PF$_6$)$_3$, 0.1 M LiTFSI, and 0.5 M *tert*-butylpyridine, in acetonitrile.

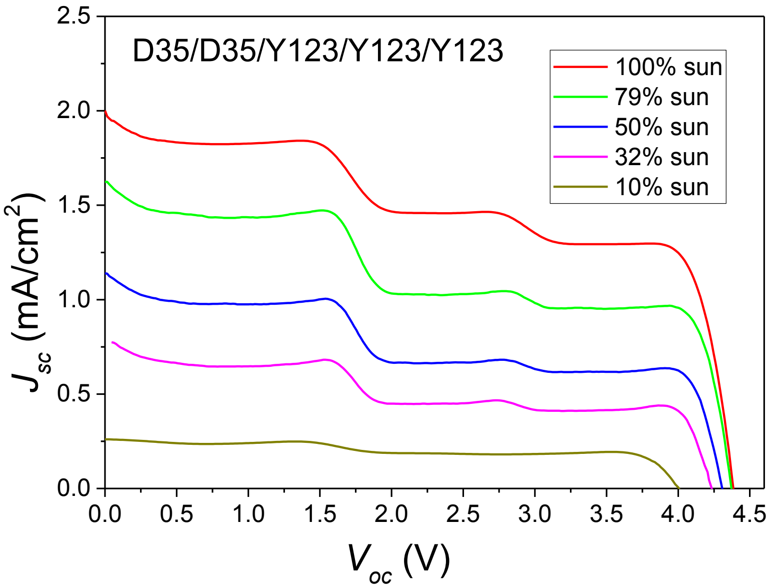


Figure S9. IV results for a 5 subcell SSM-DSC device (the final entry in Table S10) with the $Co(bpy)_3^{3+/2+}$ redox shuttle measured under different % sun values.

Table S11. Device parameters for a 5 subcell SSM-DSC device (the final entry in Table S10) with the $Co(bpy)_3^{3+/2+}$ redox shuttle measured under different % sun values.

% Sun	**V_{oc} (mV)**	**J_{sc} (mA/cm^2)**	**FF**	**PCE %**
100%	4369	1.9	57.9	4.9
79%	4322	1.6	58	4.1 (5.2%)
50%	4256	1.1	58	2.8 (5.6%)
32%	4190	0.8	59	2 (6.25%)
10%	3990	0.3	60	0.7 (7%)

Preparation of CO_2 reduction Electrodes.

Gold oxide (Au_2O_3) and Iridium oxide (IrO_2) electrodes were prepared according to literature.[11, 12] The ratio of the area of Au_2O_3 to IrO_2 electrode was (1:4.5). Briefly, for the preparation Au_2O_3 electrode, gold foil (99.95% metal basis, 0.1 mm thickness, 25*25 mm, Alfa Aesar, cut into 0.8 cm^2 (L*W, 0.4 cm *1 cm) was rinsed with diluted aqua regia mixed with deionized water (1:3), which was subsequently oxidized in 0.5 M H_2SO_4 by applying step functions, with a CHI 6054E potentiostat, by applying square pulses between 1.183 and 3.183 V versus Ag/AgCl (KCl sat.)

with a large area platinum foil counter electrode at 500 Hz (2 ms period) with 1,800,000 million cycles in a single chamber cell. Note: Extending the number of cycles to 3,600,000 million led to lower performance of the Au_2O_3 electrode and a powder to be observed to fall off the electrodes during longer cycle times. Images of the electrodes over time has been added for the 1,800,000 million cycle case to show the change in electrode color over time which was observed for high performing electrodes (Figure S10). The Au_2O_3 cathode was further rinsed with water carefully and dipped in 0.5 M $NaHCO_3$ solution for 2-3 minutes before use in the electrochemical cell. Briefly, for the anode preparation, a titanium foil (99.7%, 0.25 mm thick [3 cm*1.5 cm], Sigma Aldrich) was etched for 60 minutes in boiling 1.0 M oxalic acid, then a 0.2 M solution of H_2IrCl_6 (CAS#110802-84-1, 99.9% Ir, STREM Chemicals) in isopropanol was drop cast onto the electrode in order to cover the entire surface. The titanium foil was first dried at 70^oC for 10 minutes in air followed by calcination at 500^oC for 10 minutes in the same ovens used for the preparation of TiO_2 electrodes for DSCs (Vulcan® 3-Series model 3-550). This process was repeated three times on each side of the titanium foil. The prepared electrodes were further tested with cyclic voltammetry for current-voltage properties with a saturated CO_2 in 0.5 M $NaHCO_3$ aqueous solution. The required size 3.6 cm^2 (3 cm * 0.6 cm) was then cut from the prepared IrO_2 electrodes for use in the electrochemical cells.

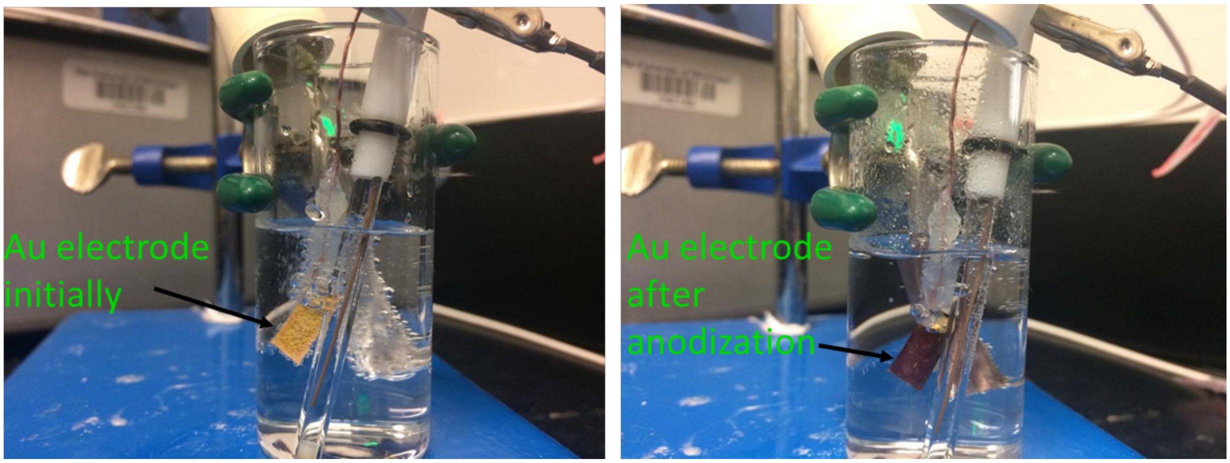


Figure S10. Au electrode initially (left) and after (right) anodization.

Electrochemical Cell (EC) and Measurements

Electrolysis was performed in a three neck flask with total volume of 61 ml. Au_2O_3 (area 0.8 cm^2) and IrO_2 (area 3.6 cm^2) electrodes were completely dipped in 25 ml of a 0.5 M $NaHCO_3$ aqueous solution along with a Ag/AgCl (CH Instruments) reference electrode sealed by septa (Suba Seal, Sigma Aldrich). CO_2 was bubbled through the solution for 30 minutes with an exit needle in place before sealing the system. The CO_2 saturated system was then activated at -0.65 V vs Ag/AgCl until a steady current was reached (~500 seconds). The CO produced during this period (and the amount of CO/current generated in the first 20 minutes of SSM-DSC powered catalysis) was subtracted from the reported CO values to ensure all catalysis was powered by the SSM-DSC device. CO, H_2 and O_2 were detected by a dual detector (TCD for H_2/O_2, FID for CO/O_2 with a methanizer) custom Agilent 7890B gas chromatograph instrument (additional details below).

After this the two electrodes, Au_2O_3 and IrO_2, were connected to a SSM-DSCs device (active area 0.5 cm^2) illuminated by a solar simulator (AAA rated for AM 1.5G sunlight) at 100 mWcm^{-2}. The continuous current flow through the photovoltaic-electrochemical (PV-EC) cell was monitored by a potentiostat (CHI 6054E) under controlled potential electrolysis (current versus time) conditions with no applied potential. During electrolysis headspace samples (300 μL) were taken at different intervals with a VICI valved syringe. The gas in the syringe was compressed to 250 μL, then with the tip of the syringed submerged in a vial of ether, the valve was open to allow the pressure to equalize to atmospheric pressure. The entire 250 μL sample was then injected onto a custom Agilent 7890B Gas Chromatograph (column, Agilent PorapakQ 6 ft, 1/8 OD) with a dual detector system (TCD and FID), a methanizer before the FID detector, and a backflush system to maintain good spectrum quality in the presence of CO_2. Quantitation of CO and methane was made using the FID detector and H_2 was quantified on the TCD detector (all calibrated using standards purchased from BuyCalGas.com).

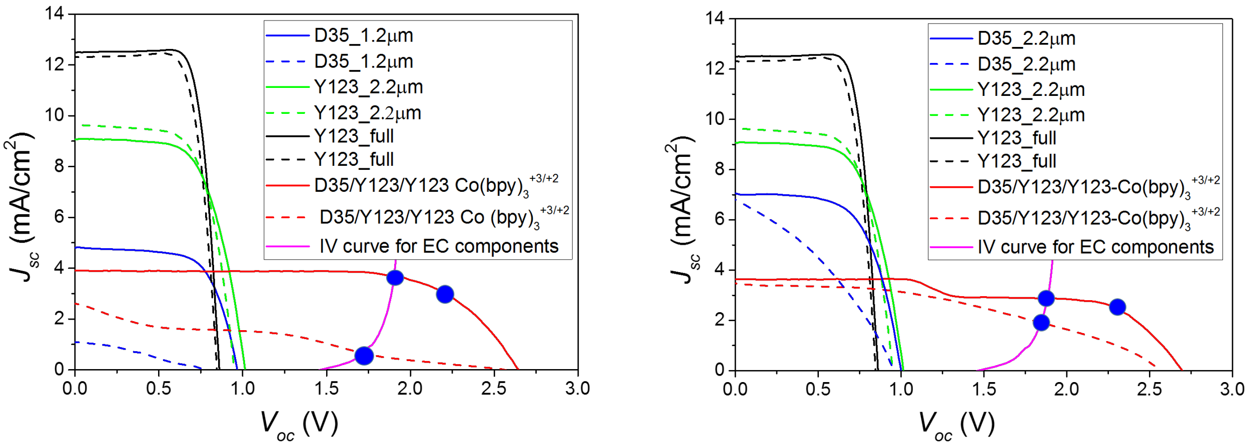


Figure S11. IV results for a three subcell SSM-DSC device and each subcell in the SSM-DSC configuration before electrolysis (solid) and after electrolysis (dotted). Left: A 1.2 μm **D35** front device was used for enhanced current matching through each subcell with a slightly lower overall voltage. Right: A 2.2 μm **D35** front device was used for a higher overall voltage with a slight lower current due to mismatching of the subcell current flow. The IV curve for the Au_2O_3/IrO_2 EC system is shown as well with the marked intersection of the IV curve. The left hand case has the EC curve intersection of the SSM-DSC curve closer to the maximum powerpoint of the SSM-DSC (marked as a blue dot with no intersecting line) leading to a higher overall solar-to-fuel efficiency. The right hand case shows a device with enhanced stability of the front cell.

Table S12. Comparison of SSM-DSC (**D35/Y123/Y123** ($Co(bpy)_3^{3+/2+}$) device parameters before and after powering CO_2 reduction.

Cell type	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF	PCE %
SSM-DSC with 1.2 μm front device				
Before electrolysis	2690	3.9	69	6.95
After electrolysis	2540	2.8	27	1.9
SSM-DSC with 2.2 μm front device				
Before electrolysis	2695	3.7	60	6.2
After electrolysis	2578	3.5	42	3.9

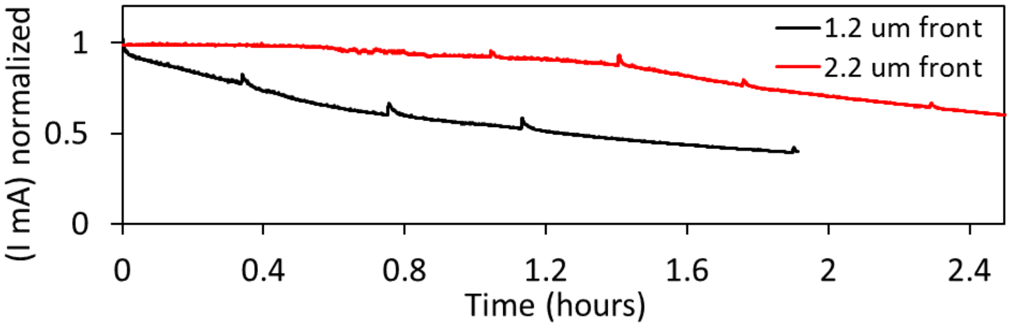


Figure S12. Current flow comparison through a PV-EC cell with different front cells.

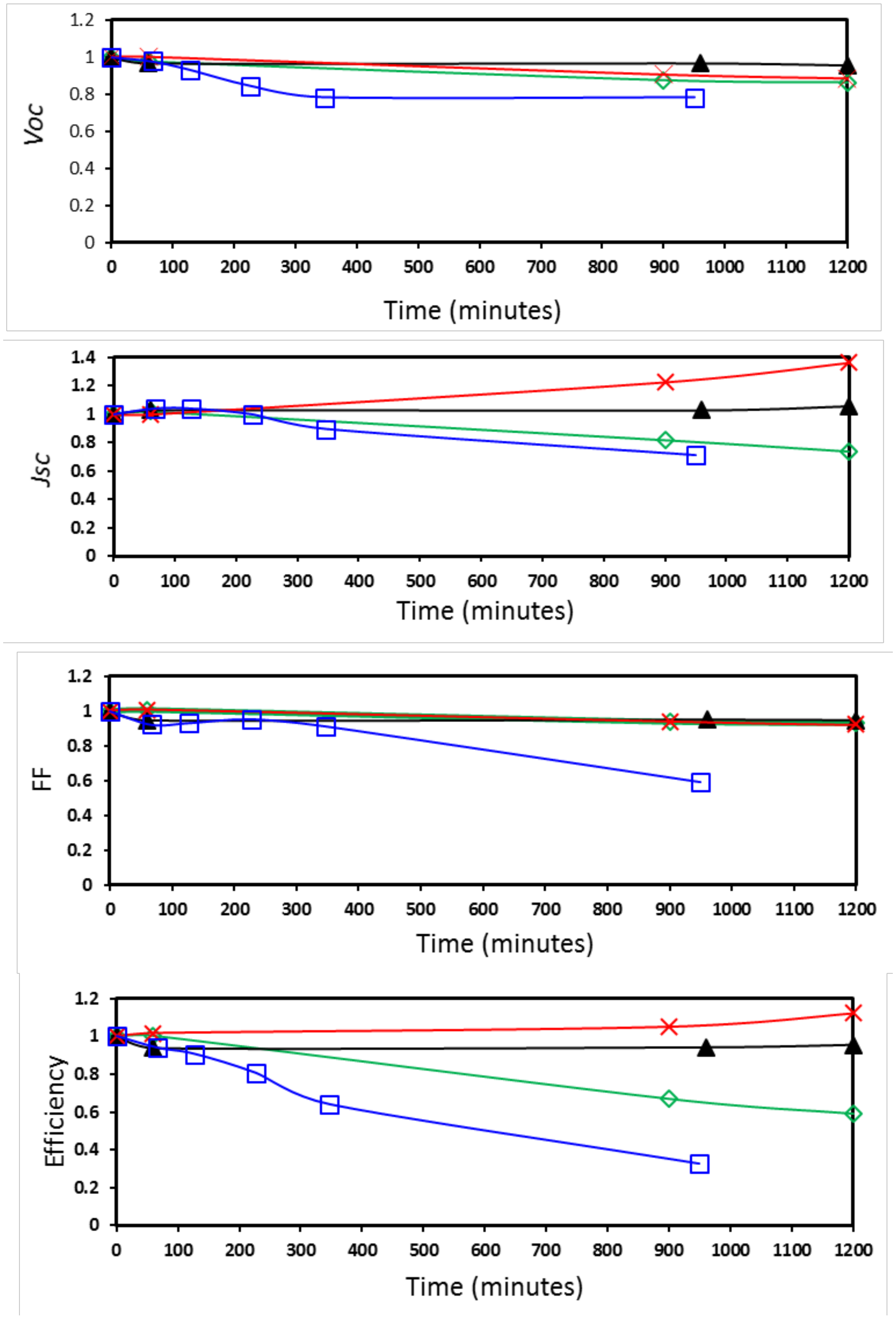


Figure S13. An early demonstration of a 1.2 μm stable front device by the application of a 385 nm UV cutoff filter and gel electrolyte. Black (triangle): gel electrolyte with the filter; Red (cross): liquid electrolyte with filter; Blue (square): liquid electrolyte no filter; Green (diamond): gel electrolyte no filter.

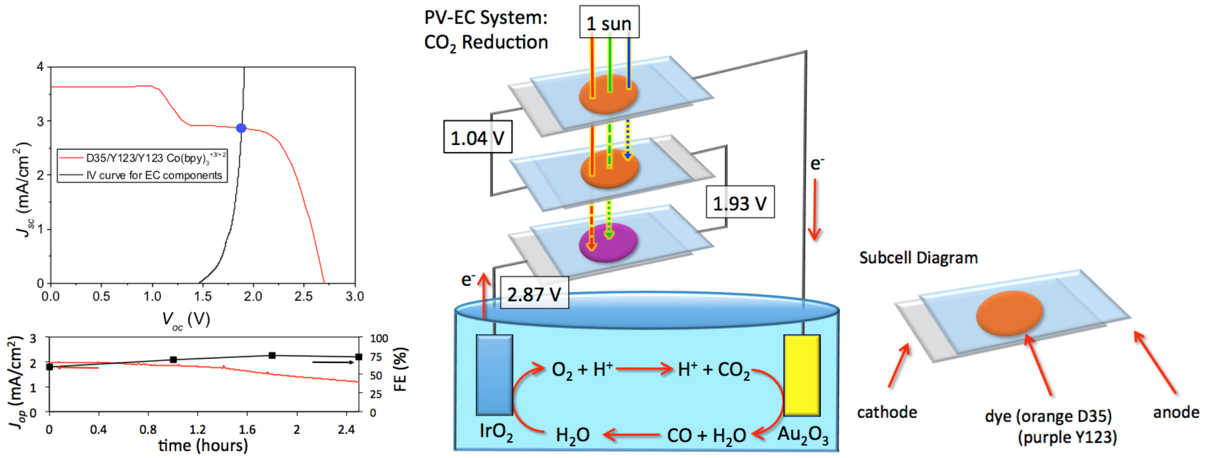


Figure S14. IV curve (left) for a PV-EC system (cartoon: middle) with a D35/Y123/Y123 device and IrO_2/Au_2O_3 electrodes. A subcell diagram is provided on the right.

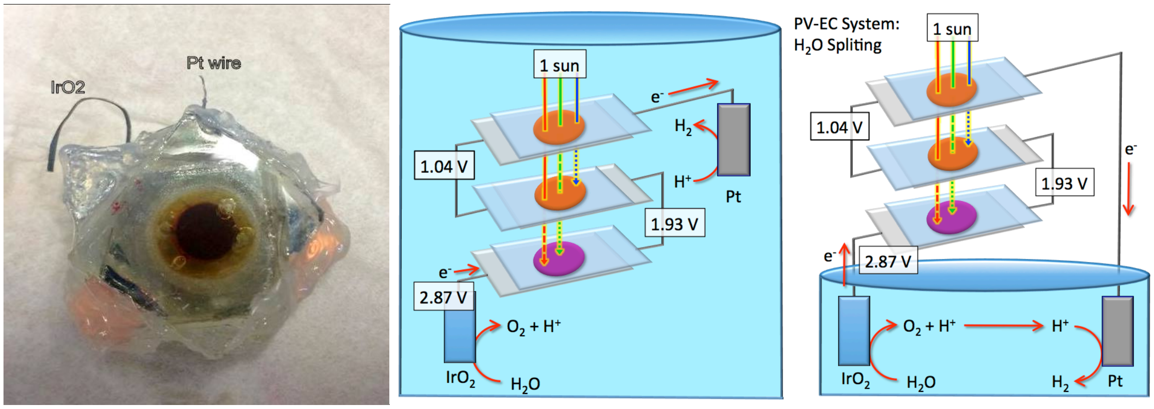


Figure S15. SSM-DSC which was dropped in H_2O in a 0.5 M $NaHCO_3$ solution (left). PV-EC system schematic cartoon submerged in water (middle). PV-EC system schematic for a non-submerged system (right). A video of this device in operation is available as a separate supplementary file.

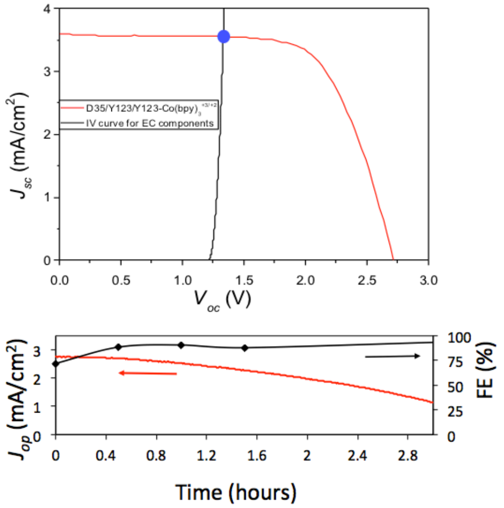


Figure S16. IV curve and current or FE versus time curve for with a D35/Y123/Y123 device and IrO_2/Pt electrodes.

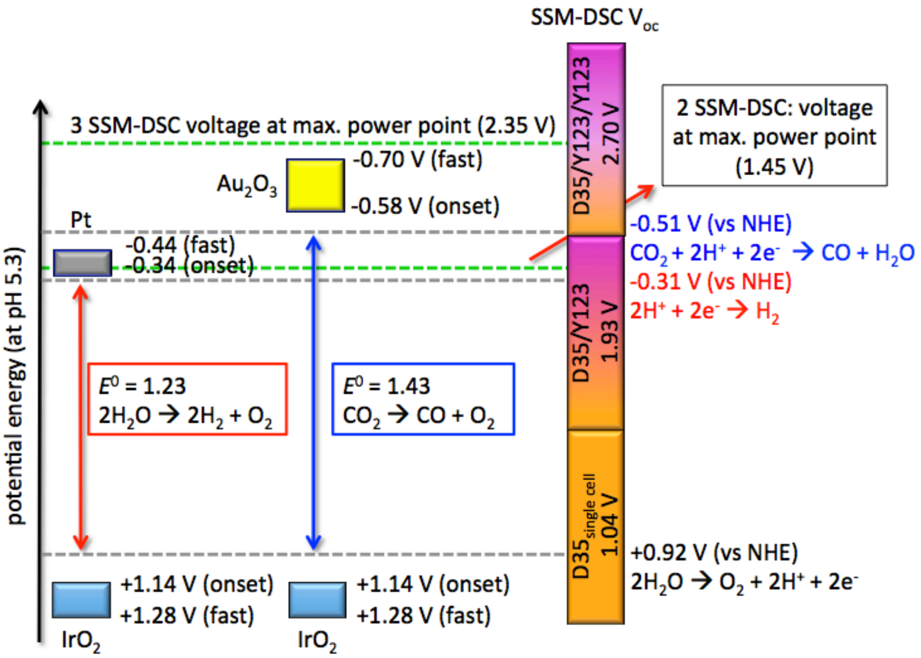


Figure S17. Energy level diagram showing the potentials needed for CO_2 or H^+ reduction coupled with water oxidation, the maximum voltage from a SSM-DSC 1-3 subcell system, and the indicated maximum power point for each SSM-DSC device.

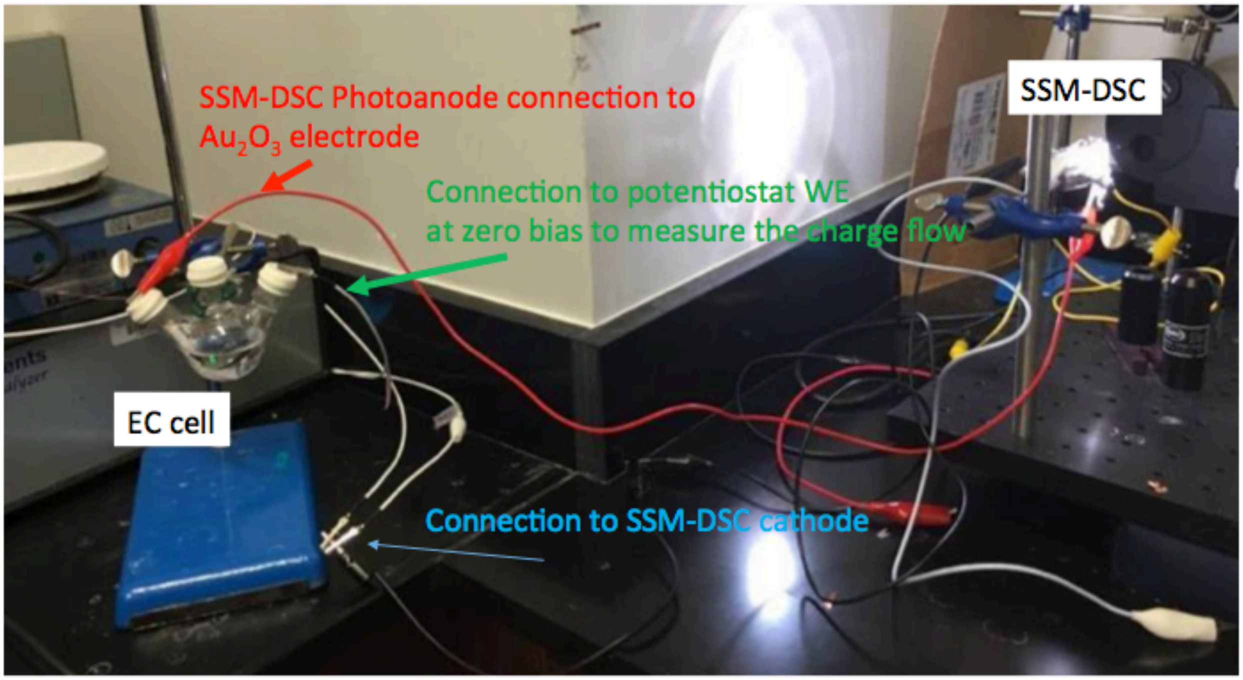


Figure S18. PV-EC setup image.

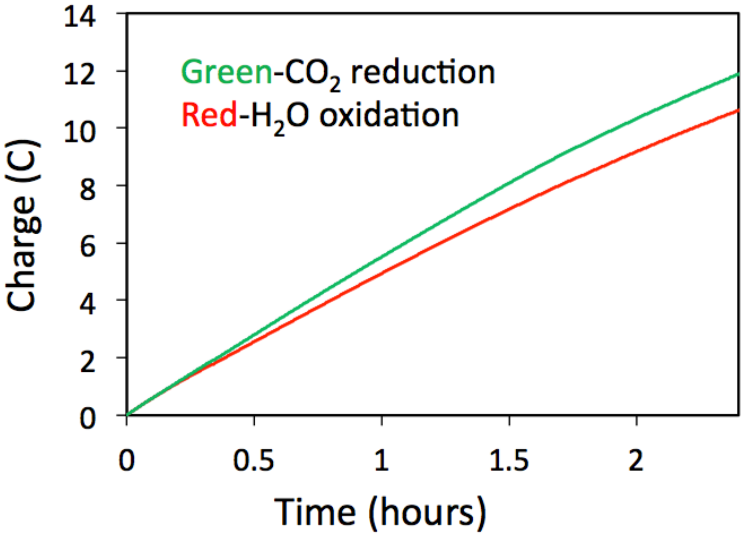


Figure S19. Charge versus time plot for H_2O splitting (red) and CO_2 reduction coupled to water oxidation (red).

GC Traces for CO_2 Reduction Coupled with Water Oxidation (Figure S14). Note: Y-axis corresponds to the FID curve. Electrolysis was run with the SSM-DSC system for 1 hour after charging the electrodes. The 1 hour reading for CO and H_2 was taken as the background. GC values are from a 250 µL injection with a calibration factor of 3.3 manually incorporated as determined from a purchased standard.

60 minutes of PV-EC electrolysis:

```
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Sample Name: Agilent_Standard_valve_syringe

    =====================================================================
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    Sample Operator : SYSTEM
    Acq. Instrument : Agilent                        Location : Vial 1
    Injection Date  : 4/11/2017 3:02:13 PM
                                                   Inj Volume : Manually
    Acq. Method     : C:\CHEM32\2\METHODS\START.M
    Last changed    : 3/13/2017 3:12:26 PM by SYSTEM
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/11/2017 3:27:22 PM by SYSTEM
                      (modified after loading)
```

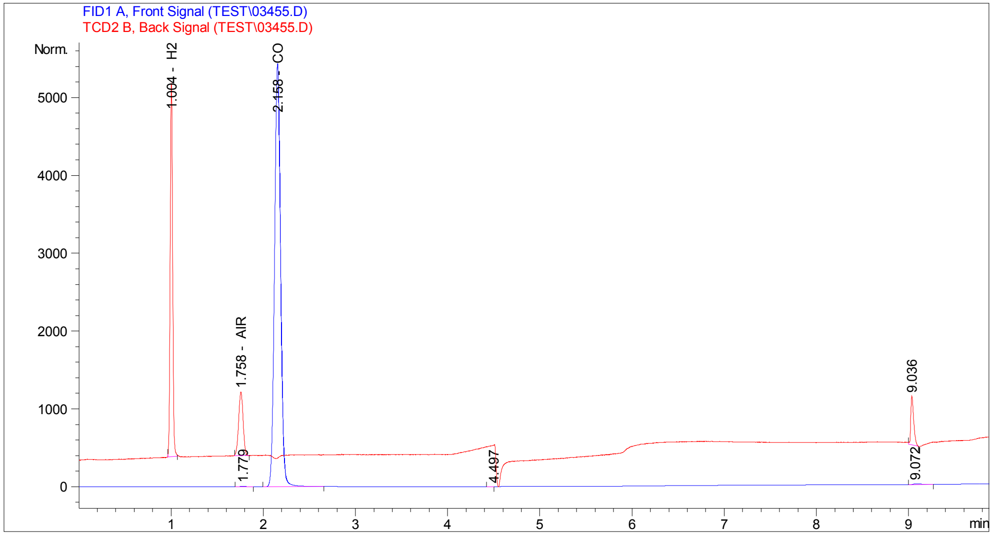

```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/11/2017 10:15:18 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [pA*s]               [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.158 BB     2.48416e4  1.15369e-1 2865.95587    CO
      4.159            -          -          -         CH4

    Totals :                             2865.95587


Agilent 4/11/2017 3:27:26 PM SYSTEM                              Page    1 of 2
```

100 minutes of PV-EC electrolysis:

```
Data File C:\CHEM32\2\DATA\SNAPSHOT.D
Sample Name:

    =====================================================================
    Acq. Operator   : SYSTEM
                                                  Location : Vial 1
    Injection Date  : 4/11/2017 3:26:35 PM
    Acq. Method     : START.M
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/11/2017 3:31:09 PM by SYSTEM
                      (modified after loading)
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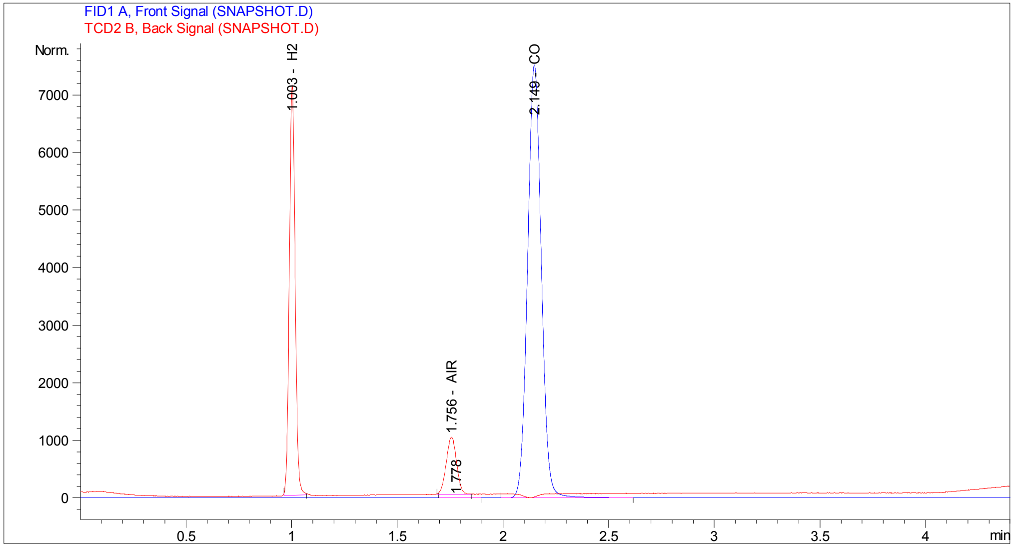

```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/11/2017 10:15:18 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area      Amt/Area     Amount   Grp   Name
     [min]          [pA*s]                  [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.149 BB S    3.39128e4  1.15369e-1 3912.49498    CO
      4.159            -          -          -         CH4

    Totals :                              3912.49498
```

215 minutes of PV-EC electrolysis:

```
Data File C:\CHEM32\2\DATA\SNAPSHOT.D
Sample Name:

    =====================================================================
    Acq. Operator   : SYSTEM
                                                  Location : Vial 1
    Injection Date  : 4/11/2017 4:13:15 PM
    Acq. Method     : START.M
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/11/2017 4:18:17 PM by SYSTEM
                      (modified after loading)
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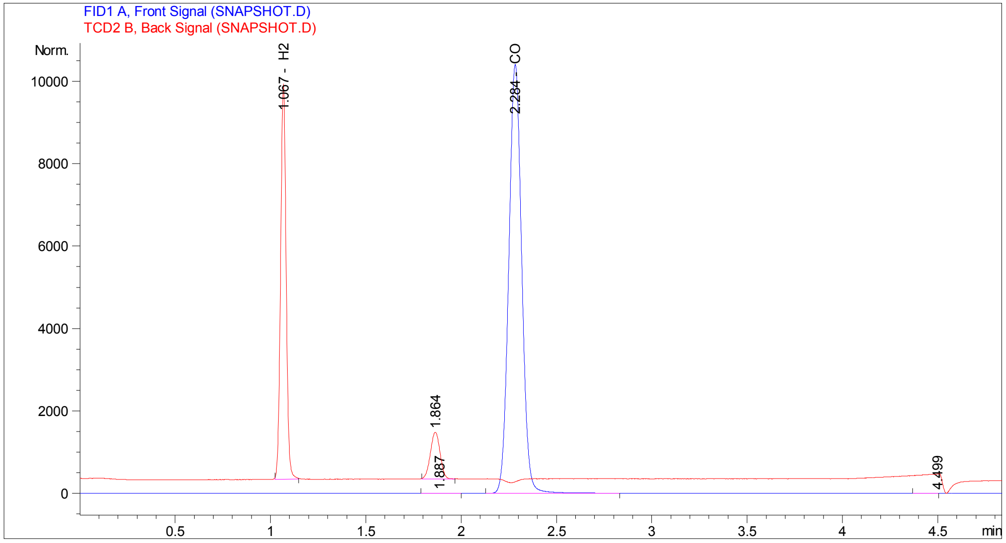
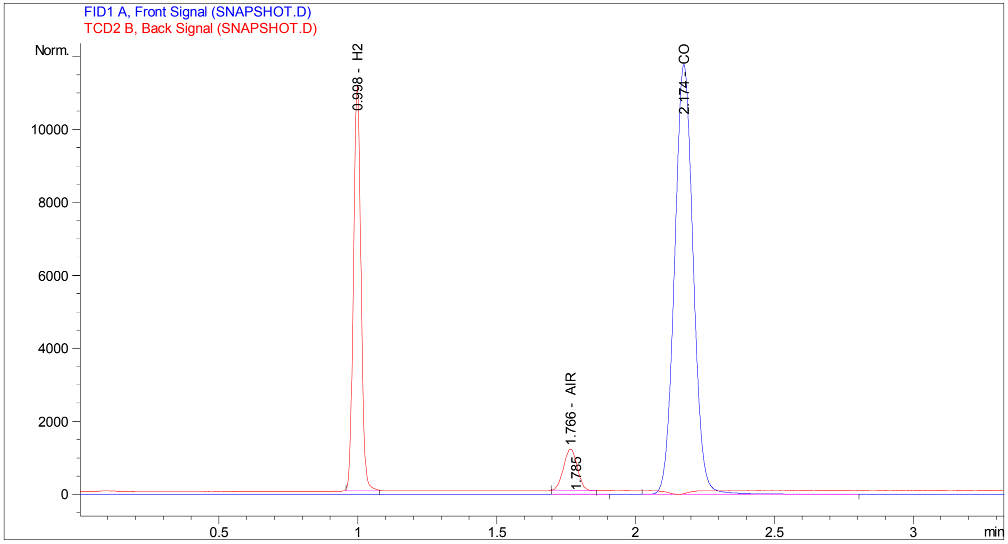


```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/11/2017 10:15:18 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [pA*s]                [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.284 BB S   4.89637e4  1.15369e-1 5648.90846    CO
      4.159            -          -          -         CH4

    Totals :                             5648.90846



Agilent 4/11/2017 4:18:21 PM SYSTEM                                    Page    1 of 2
```

250 minutes of PV-EC electrolysis:

```
Data File C:\CHEM32\2\DATA\SNAPSHOT.D
Sample Name:

    =====================================================================
    Acq. Operator   : SYSTEM
                                                  Location : Vial 1
    Injection Date  : 4/11/2017 4:50:14 PM
    Acq. Method     : START.M
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/11/2017 4:53:45 PM by SYSTEM
                      (modified after loading)
```

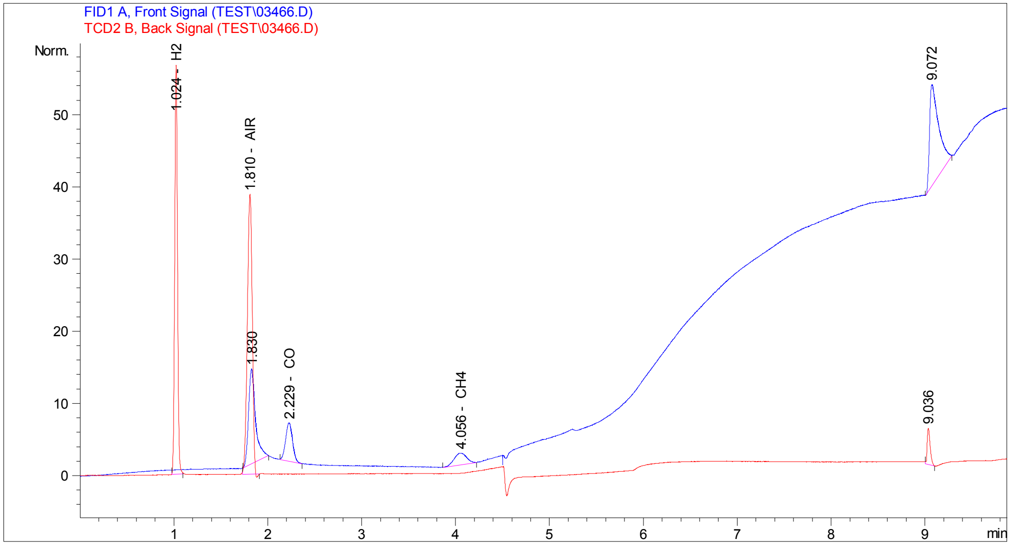


```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/11/2017 10:15:18 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [pA*s]              [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.174 BB S   5.49914e4 1.15369e-1 6344.31695    CO
      4.159            -          -          -        CH4

    Totals :                            6344.31695
```

GC Traces for Proton Reduction Coupled with Water Oxidation. Note: Y-axis corresponds to the TCD curve. Electrolysis was run with the SSM-DSC system for 1 hour after charging the electrodes. The 1 hour reading for H_2 was taken as the background. GC values are from a 250 µL injection and manually calibrated via a purchased standard.

20 Minutes:

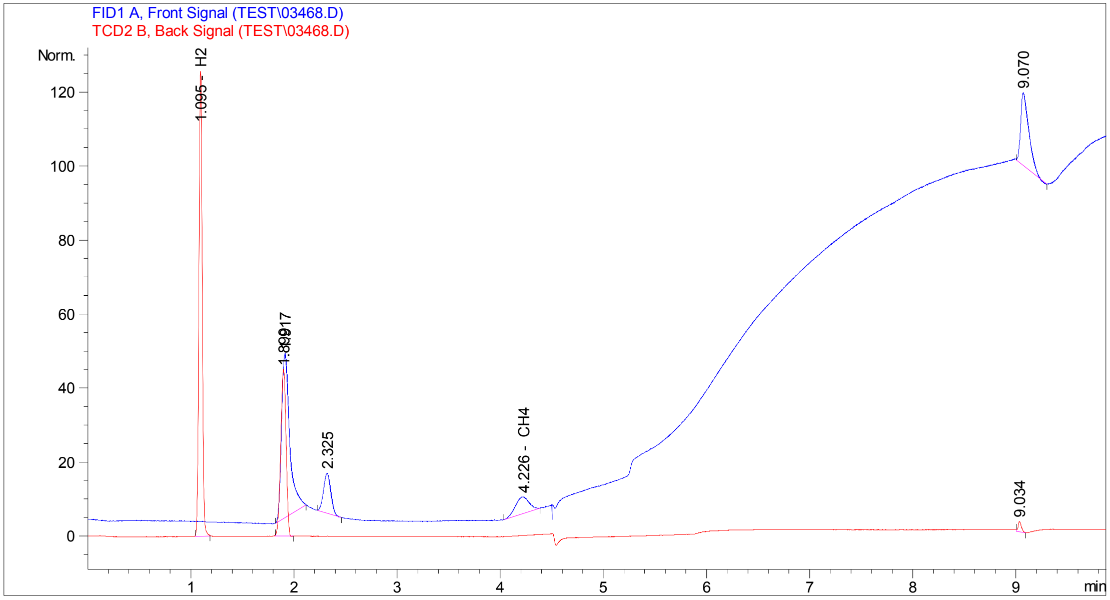
```
Data File C:\CHEM32\2\DATA\TEST\03466.D
Sample Name: Agilent_Standard_valve_syringe

    =====================================================================
    Acq. Operator   : SYSTEM
    Sample Operator : SYSTEM
    Acq. Instrument : Agilent                          Location : Vial 1
    Injection Date  : 4/12/2017 11:19:46 AM
                                                     Inj Volume : Manually
    Acq. Method     : C:\CHEM32\2\METHODS\START.M
    Last changed    : 3/13/2017 3:12:26 PM by SYSTEM
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/12/2017 11:41:32 AM by SYSTEM
                      (modified after loading)
```



```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/12/2017 9:40:46 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area      Amt/Area    Amount   Grp   Name
     [min]          [pA*s]                 [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.229 BB       18.09289 1.15369e-1    2.08736     CO
      4.056 BB        9.94288 1.40742e-1    1.39938     CH4

    Totals :                                3.48674



Agilent 4/12/2017 11:41:37 AM SYSTEM                                      Page    1 of 2
```

45 Minutes:

```
Data File C:\CHEM32\2\DATA\TEST\03468.D
Sample Name: Agilent_Standard_valve_syringe

    =====================================================================
    Acq. Operator   : SYSTEM
    Sample Operator : SYSTEM
    Acq. Instrument : Agilent                          Location : Vial 1
    Injection Date  : 4/12/2017 11:44:23 AM
                                                    Inj Volume : Manually
    Acq. Method     : C:\CHEM32\2\METHODS\START.M
    Last changed    : 3/13/2017 3:12:26 PM by SYSTEM
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/12/2017 11:57:45 AM by SYSTEM
                      (modified after loading)
```



```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/12/2017 9:40:46 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area      Amt/Area    Amount   Grp   Name
     [min]          [pA*s]                 [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.193            -          -          -        CO
      4.226 BB      12.17270 1.40742e-1    1.71320    CH4

    Totals :                               1.71320
```

70 Minutes:

```
Data File C:\CHEM32\2\DATA\TEST\03469.D
Sample Name: Agilent_Standard_valve_syringe

    =====================================================================
    Acq. Operator   : SYSTEM
    Sample Operator : SYSTEM
    Acq. Instrument : Agilent                          Location : Vial 1
    Injection Date  : 4/12/2017 12:10:29 PM
                                                     Inj Volume : Manually
    Acq. Method     : C:\CHEM32\2\METHODS\START.M
    Last changed    : 3/13/2017 3:12:26 PM by SYSTEM
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/12/2017 12:33:25 PM by SYSTEM
                      (modified after loading)
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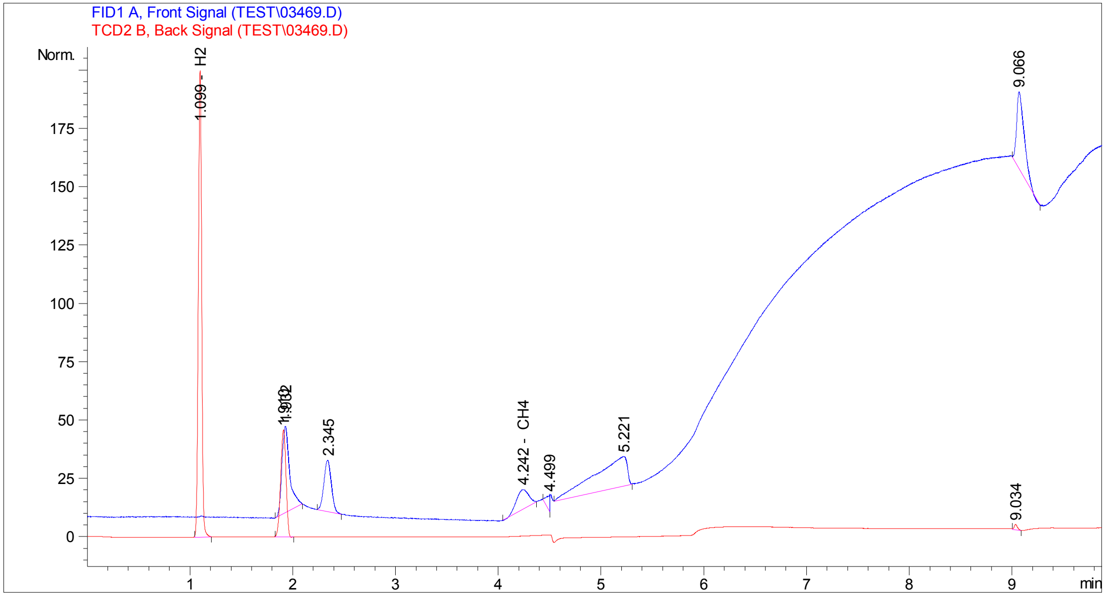

```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/12/2017 9:40:46 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area      Amt/Area     Amount   Grp   Name
     [min]          [pA*s]                  [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.193             -          -           -         CO
      4.242 BB      10.48458 1.40742e-1    1.47562      CH4

    Totals :                               1.47562
```

90 Minutes:

```
Data File C:\CHEM32\2\DATA\TEST\03470.D
Sample Name: Agilent_Standard_valve_syringe

    =====================================================================
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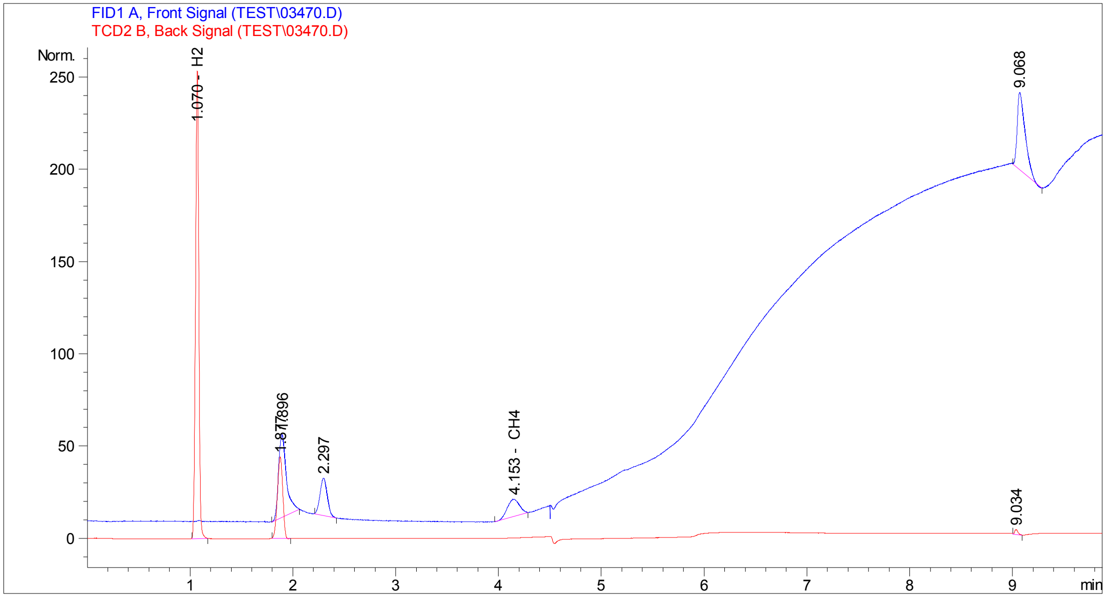
    Sample Operator : SYSTEM
    Acq. Instrument : Agilent                        Location : Vial 1
    Injection Date  : 4/12/2017 12:33:00 PM
                                                   Inj Volume : Manually
    Acq. Method     : C:\CHEM32\2\METHODS\START.M
    Last changed    : 3/13/2017 3:12:26 PM by SYSTEM
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/12/2017 1:10:25 PM by SYSTEM
                      (modified after loading)
```



```
    =====================================================================
                          External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/12/2017 9:40:46 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area      Amt/Area    Amount   Grp   Name
     [min]          [pA*s]                 [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.193             -          -          -         CO
      4.153 BB       11.51902 1.40742e-1    1.62120     CH4

    Totals :                                1.62120
```

200 Minutes:

```
Data File C:\CHEM32\2\DATA\SNAPSHOT.D
Sample Name:

    =====================================================================
    Acq. Operator   : SYSTEM
                                                  Location : Vial 1
    Injection Date  : 4/12/2017 2:17:29 PM
    Acq. Method     : START.M
    Analysis Method : C:\CHEM32\2\METHODS\START.M
    Last changed    : 4/12/2017 2:21:32 PM by SYSTEM
                      (modified after loading)
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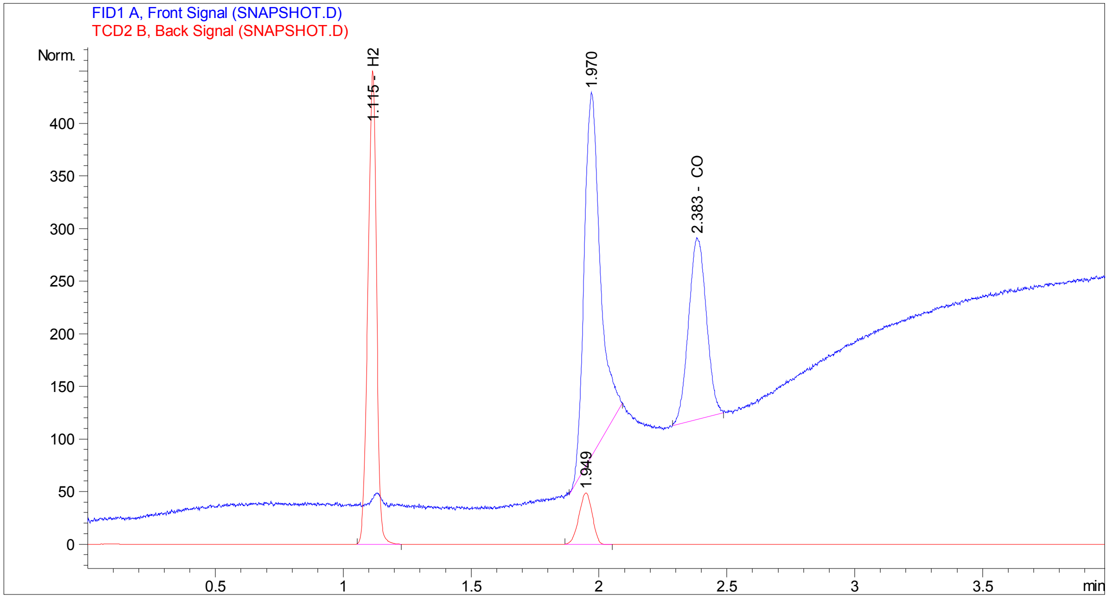

```
    =====================================================================
                         External Standard Report
    =====================================================================

    Sorted By             :      Signal
    Calib. Data Modified  :      4/12/2017 9:40:46 AM
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A, Front Signal

    RetTime  Type     Area     Amt/Area    Amount   Grp   Name
     [min]          [pA*s]                 [ng/ul]
    -------|------|----------|----------|----------|--|------------------
      2.383 BB       10.30921 1.15369e-1    1.18937    CO
      4.159             -          -          -        CH4

    Totals :                                1.18937
```

References:

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