Precious Metal-Free Solar-to-Fuel Generation: SSM-DSCs Powering Water Splitting with NanoCOT and NiMoZn Electrocatalysts

*Hammad Cheema,[a] Jonathon Watson,[a] Pravin S. Shinde,[b] Roberta R. Rodrigues,[a] Shanlin Pan,[b] and Jared H. Delcamp[a,]**

[a]Coulter Hall, Department of Chemistry and Biochemistry, University of Mississippi, University, MS, 38677, United States.

[b]Department of Chemistry and Biochemistry, The University of Alabama, Tuscaloosa, Alabama 35487, United States.

*corresponding author

*Jared H. Delcamp, delcamp@olemiss.edu

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1. General Procedures

All commercially obtained reagents were used as received. Absorbance spectra were measured with a Cary 5000 UV−Vis−NIR spectrophotometer. Cyclic voltammetry curves were measured with a CH Instruments electrochemical analyzer (CHI-600E). **D35** and **Y123** were purchased from Dyenamo, Sweden, and used as it is. Co(bpy)$_3^{3+/2+}$ and Co(bpy-pz)$_2^{3+/2+}$were prepared by following the literature procedures.[1, 2] **AP25** was prepared according to literature reported proceedures.[3] 1H,1H,2H,2H-perfluorooctyltrimethoxysilane (PFTS) was purchased from Beantown Chemical Company. Chenodeoxycholic acid (CDCA) was purchased from Chem-Impex International. TEC 10, TEC15, and TEC7 were all purchased from Hartford Glass Company, Indiana, USA. Amorphous fluoropolymer CYTOP (CTL-809) and solvent (CT-Sol.180) were purchased from Asahi Glass Company, Japan. Graphene Nanoplatelets (GNP) were purchased from Cheap Tubes (Cheaptubes.com, SKU: 05017) and used as it is.

2. Sensitizer Chemical Structures

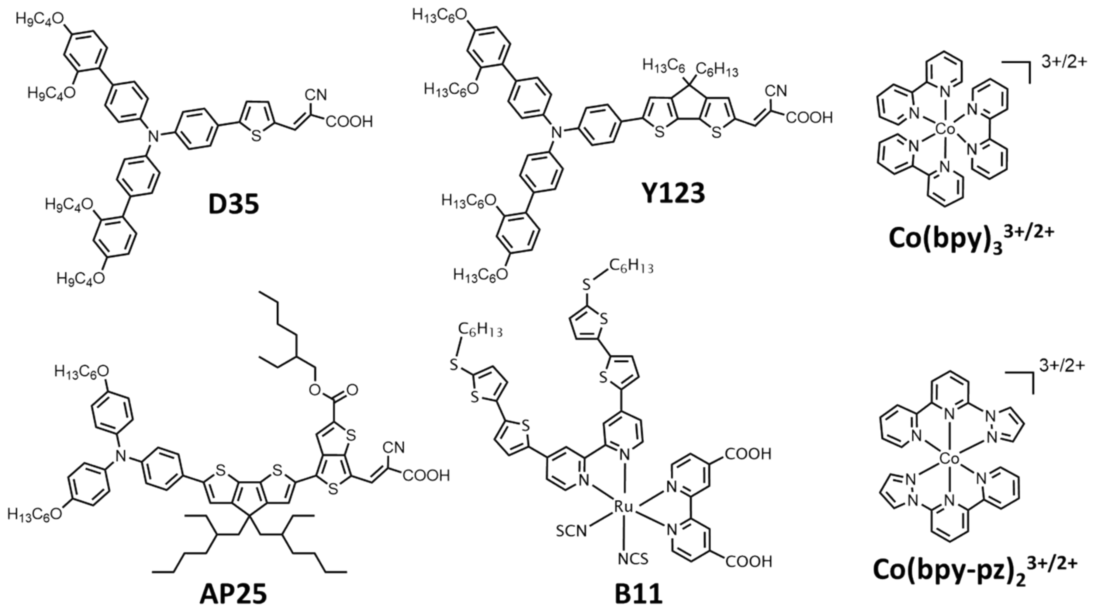

Figure S1. Chemical structures of sensitizers **D35**, **Y123**, and **AP25.**

3. Sensitizer Optical and Electrochemical Data

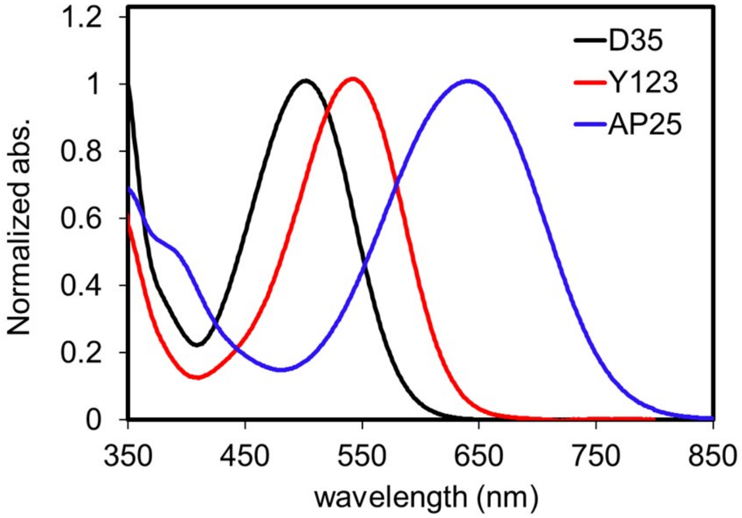

Figure S2. Normalized absorption comparison of **D35**, **Y123**, and **AP25**.

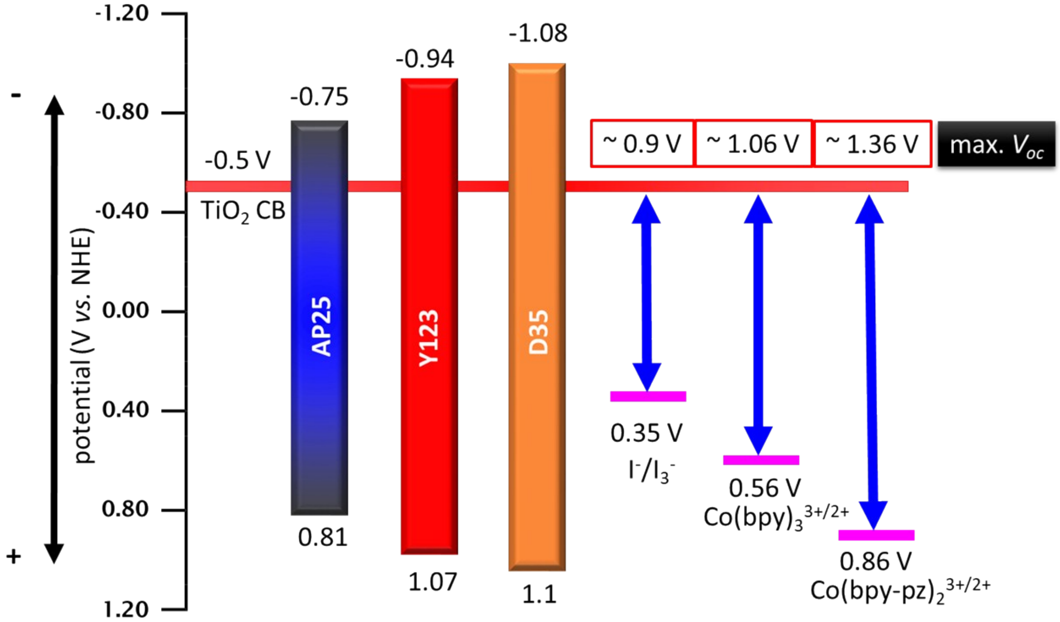

Figure S3. Energy level diagram comparing sensitizers and redox shuttles.[4]

Table S1. Comparison of optical and electrochemical data for **D35, Y123**, and **AP25.**

Dye	λ_{max} [a] (nm)	λ_{onset} [b] (nm)	ε [a] (M^{-1} cm^{-1})	$E_{(S+/S)}$ [c] (V)	$E_{(S+/S^*)}$ [d] (V)	E_g^{opt} [e] (eV)
D35	500	570	31000	1.04	-1.14	2.18
Y123	540	650	49000	0.92	-1.09	2.01
AP25	660	780	30000	0.81	-0.75	1.56

[a]Measured in CH_2Cl_2. [b]Onset values taken from the x-intercept of the downward line of best fit of the absorbance curve on the low energy side. [c]Measured with a 0.1 M Bu_4NPF in CH_2Cl_2 solution using a glassy carbon working electrode, platinum reference electrode, and platinum counter electrode with ferrocene as an internal standard. Values are reported versus NHE. [d] $E_{(S+/S^*)}$ was calculated from the equation $E_{(S+/S^*)} = E_{(S+/S)} - E_g^{opt}$. [e]Estimated from the onset of the absorption curve in CH_2Cl_2. Conversion from nanometers to eV was calculated by $E_g^{opt} = 1240/\lambda_{onset}$. [f] **D35**, **Y123**, and **AP25** data was taken from previous reports.[4, 5]

4. Device Measurements and Assembly Procedures

4.1. 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. Before 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 a 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.

4.2. Device Fabrication

Photoanode preparation: All the DSCs were prepared the same way as is reported previously.[6, 7] **D35** and **Y123** devices were prepared without the scattering layer on TEC 15 FTO glass (15 Ω/sq. sheet resistance: FTO) which 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 10 min at room temperature. The electrodes were rinsed with water, sonicated in acetone 10 min, and sonicated in ethanol for 10 min. The electrodes were then placed under UV/ozone for 15 min (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 °C). The submerged substrates (conductive side up) were heated for 30 min at 70 ^{o}C. After heating, the substrates were rinsed first with water then with ethanol. Mesoporous P30 TiO_2 layer (cobalt paste used for **D35** and **Y123** devices, particle size: 30 nm, Dyenamo, DN-GPS-30TS, >99% anatase) was screen printed from a Sefar screen (54/137–64W) resulting in 3 µm (diluted 1.5:1 paste:terpineol) or Sefar screen (90/230-48W) resulting in 1.5 µm (diluted 1.5:1 paste:terpineol) thickness on average for each print. Mesoporous P18 TiO_2 (iodine paste for **AP25+D35** devices, particle size: 18 nm, Dyesol or Great Cell Solar, 18NR-T Transparent Titania Paste) was screen printed from a Sefar screen (54/137–64W) resulting in 5 µm thickness on average for each print. 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 the **AP25** 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 min at 125 ^{o}C, and the thickness was measured with a profilometer (Alpha-Step D-500 KLA Tencor). The substrate was then sintered with progressive heating from 125 ^{o}C (5 min ramp from room temperature, 5 min hold) to 325 ^{o}C (15 min ramp from 125 ^{o}C, 5 min hold) to 375 ^{o}C (5 min ramp from 325 ^{o}C, 5 min hold) to 450 ^{o}C (5 min ramp from 375 ^{o}C, 15 min hold) to 500 ^{o}C (5 min ramp from 450 ^{o}C, 15 min hold) using a programmable furnace (Vulcan® 3-Series model 3-550). All reported device thicknesses were measured postsintering. The cooled, sintered photoanode was soaked 30 min at 70 ^oC in a 40 mM $TiCl_4$ water solution and heated at 40 ^oC min^{-1} to 500 ^oC and held at 500 ^oC for 30 min and then cooled down to room temperature before sensitization. The complete working electrode was prepared by immersing the TiO_2 films in respective dye solutions. Such as **D35** dye solution (0.3 mM, 1:1 (ACN:*tert*-butanol)), with 10x (3 mM) of chenodeoxycholic acid (CDCA), **Y123** dye solution (0.2 mM, 1:1 (ACN:*tert*-butanol)) with 50x CDCA, and for co-sensitized devices, 0.3 mM total dye concentration with **AP25:D35** (2:1) and the optimized amount of CDCA was (9 mM) in ACN:*tert*-butanol was employed.[4, 8] The electrodes were immersed in these dye solutions at room temperature for 6 hours for **D35** and **Y123**, but overnight for **AP25+D35**.

Counter Electrode Preparation: Two holes were drilled through the conducting side to the insulating side of 2 x 2 cm squares of TEC 7 FTO glass (7 Ω/sq. sheet resistance) for **AP25+D35** cells, 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 min and dried at 400 °C for 15 min. For GNP electrodes: A thin layer of GNP-suspension (Cheaptubes.com, Graphene Nanoplatelets, SKU: 05017) was drop cast on the conductive side. For preparation of the GNP suspension, 1 mg/ml of GNP was dissolved in laboratory grade 2-propanol by sonication for 20 min in a Kendal ultrasonic cleaner (Model HB-S-49 DHT). After that, 2 to 3 drops of the GNP suspension was drop cast. The solvent was allowed to evaporate completely (approx. 10 min) with further cleaning of FTO with Kimwipe by wiping the surface. The electrodes were then cured at 400 °C for 15 min and used after cooling.

PEDOT electrodes: PEDOT electrodes were used only in the experiments where **AP25+D35** was the final cell. PEDOT electrodes were prepared following the previously reported procedure.[9] 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 min. 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 s, cathodic time of 0.005 s, anodic time 70 s, with initial polarity anodic, data storage interval as 0.1 s 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 min at 125 ^{o}C before use.

Dye-sensitized Solar Cell assembly: The photoanode and counter electrode were sealed with either a 25 μm thick (**D35** and **Y123** devices) or 60 μm thick hot melt gasket (Surlyn, Solaronix, "Meltonix 1170") by heating the system at 130 °C under a pressure of 0.2 psi for 1 min with a sealing machine (Dyenamo, product DN-HM01). The respective 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 s both for full and thin devices. Finally, soldered contacts were added with an 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.

4.3. Preparation of Cytop Solution and Deposition by Spin Coating

Cytop (CTL-809) was dissolved in 18 wt% concentration of CT-Sol.180 on a hotplate, which was set at 110 °C. The mixture was stirred for 5 min at 110 °C. After this, the prepared mixture was spin-coated (Laurel Model WS-650MZ-23) on the FTO in a continuous two-step coating process with 500 rpm for 10 s and 1000 rpm for 20 s. In the end, the FTO substrates were cured at 200 °C for 1 h under ambient conditions in a programmable furnace (Vulcan® 3-Series model 3-550).

4.4. Photoanode Surface Treatment

PFTS treatment: **D35** 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 °C. The electrodes were rinsed with hexanes and assembled as described above.

4.5. Transmittance Studies

Transmittance spectra were measured with a Cary 5000 UV-Vis spectrometer first by running a baseline with an FTO (TEC15) coated substrate in both the sample and standard compartment. All samples were then measured against TEC15 as a standard.

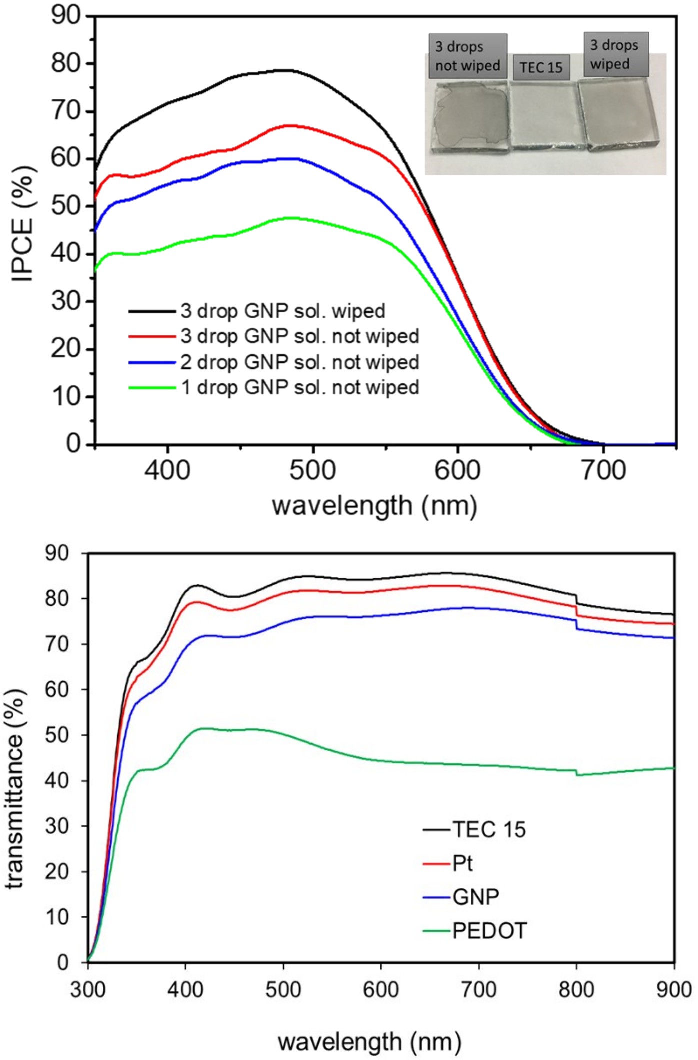

Figure S4. Comparison of the IPCE response for individual **Y123** devices given in the Table S2 (top) inset shows the electrodes with and without wiping GNP, (bottom) transmittance comparison of optimized GNP, Pt, PEDOT, and TEC 15 glass only.

Table S2. Summary of a DSC device performance parameters during GNP optimization.[a]

GNP sol. amount	*Voc* (mV)	*Jsc* (mA cm^{-2})	FF (%)	PCE (%)
1 drop not wiped	822	7.5	60	3.6
2 drops not wiped	811	8.9	60	4.2
3 drops not wiped	661	10.1	52	3.5
3 drops wiped	818	11.9	68	6.7

[a] Electrolyte is Co(bpy)$_3^{3+/2+}$: 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 4-*tert*-butylpyridine (TBP), in acetonitrile.The TiO$_2$ thickness was 3 µm for all the devices with **Y123** as the dye. All the GNP electrodes were prepared on TEC 15 glass and cured at 140 °C for 15 minutes. All the devices had a CYTOP anti-reflective coating.

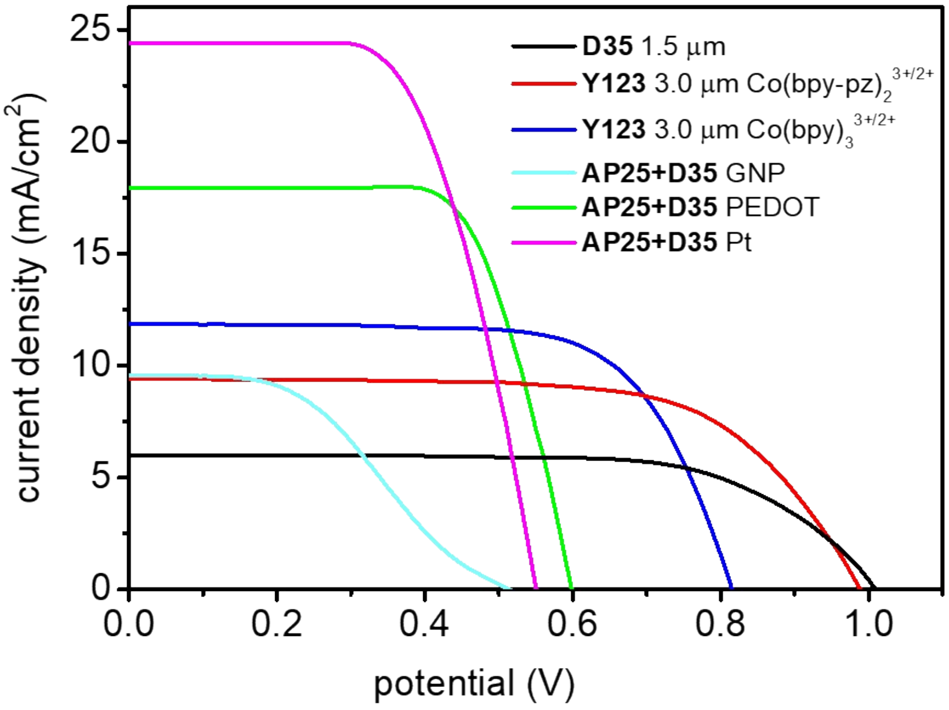

Figure S5. Comparison of *J*-*V* curves for individual devices given in Table S3.

Table S3. Summary of DSC device performance parameters.[a]

Dye (TiO_2 thickness)	Electrolyte/C.E.	*V*oc (mV)	*J*sc (mA cm^{-2})	FF (%)	PCE (%)
D35 (1.5 μm)	Co(bpy-pz)$_2^{3+/2+}$/GNP	1004 ± 5	5.7 ± 0.3	64 ± 1	3.7 ± 0.3
Y123 (3 μm)	Co(bpy-pz)$_2^{3+/2+}$/GNP	963 ± 26	9.4 ± 0.1	68 ± 1	6.2 ± 0.1
	Co(bpy)$_3^{3+/2+}$/GNP	791 ± 20	11.6 ± 0.2	71 ± 1	6.5 ± 0.2
AP25+**D35** (15 μm)	I_3^-/I^-/GNP	504 ± 9	9.3 ± 0.4	44 ± 2	2.2 ± 0.1
AP25+**D35** (15 μm)	I_3^-/I^-/PEDOT	608 ± 11	18.0 ± 0.5	70 ± 1	7.5 ± 0.1
AP25+**D35** (15 μm)	I_3^-/I^-/Pt	569.5±11	23.7±0.7	63 ± 0.5	8.3 ± 0.2

[a] Device performances under AM 1.5G irradiation. For **AP25+D35** devices TiO_2 electrodes are comprised of a 15 μm film active layer of 18 nm TiO_2 nanoparticles with a 5 μm film scattering layer of >100 nm TiO_2 nanoparticles on top. The I_3^-/I^- electrolyte is: 1.0 M DMII (1,3-dimethylimidazolium iodide), 0.03 M I_2, 0.1 M GuNCS (guanidinium thiocyanide). 0.7 M LiI (lithium iodide) and 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile:valeronitrile (85:15,v/v) solvent. Co(bpy-pz)$_2^{3+/2+}$ electrolyte had the following concentrations: 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 4-*tert*-butylpyridine (TBP) in acetonitrile and 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 4-*tert*-butylpyridine (TBP) in acetonitrile. All the devices had CYTOP antireflective coating.

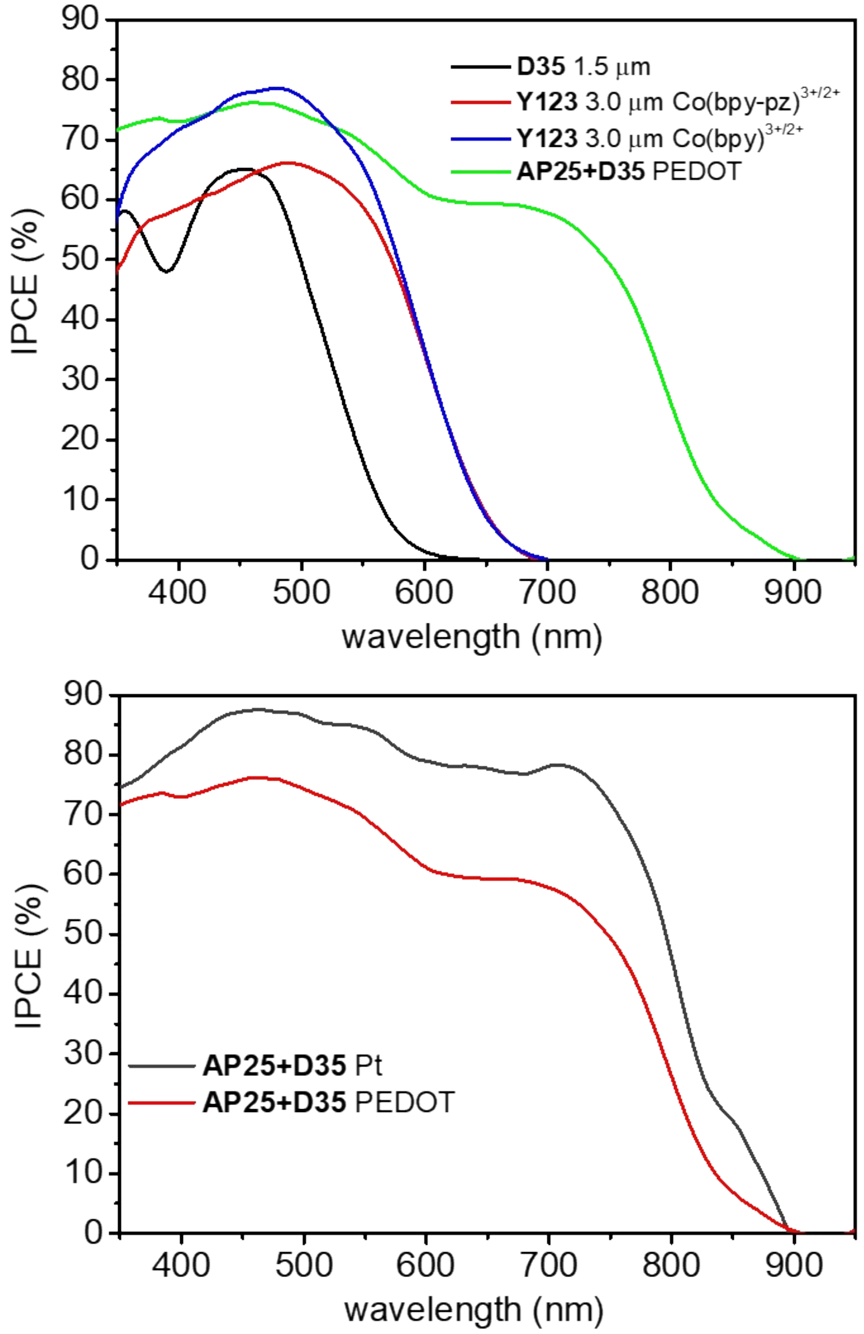

Figure S6. Comparison of IPCE response for individual devices given in Table S3.

Table S4. Summary of DSCs device data for **D35**, **Y123**, and co-sensitized **AP25+D35** dyes.[a]

Dye (TiO$_2$ thickness)/Redox	Position	V_{oc} (mV)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
D35 (1.5 μm)/Co(bpy-pz)$_2^{3+/2+}$	front	1004 ± 5	5.7 ± 0.3	64 ± 1	3.7 ± 0.3
Y123 (3.0 μm)/Co(bpy-pz)$_2^{3+/2+}$	itself	963 ± 26	9.4 ± 0.1	68 ± 1	6.2 ± 0.1
	2nd	985 ± 19	3.3 ± 0.1	71 ± 0	2.3 ± 0.1
AP25+D35 (15 μm)/(I$^-$/I$_3^-$)	itself	608 ± 11	18 ± 0.5	70 ± 1	7.5 ± 0.1
	3rd	577 ± 20	4.9 ± 0.1	74 ± 1	2.3 ± 0.1
D35/Y123/AP25+D35 CYTOP	**SSM-DSC**	**2518 ± 13**	**5.3 ± 0.1**	**50 ± 1**	**6.8 ± 0.2**

[a] Device assembly details and redox shuttles are the same as given under Table S3.

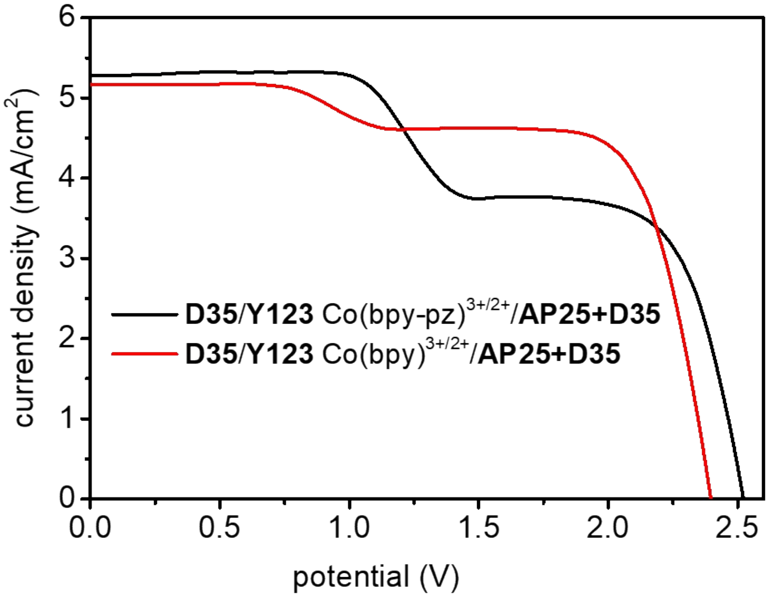

Figure S7. Comparison of the *J-V* curves of SSM-DSC devices with Co(bpy-pz)$_2^{3+/2+}$ or Co(bpy)$_3^{3+/2+}$ as a redox shuttle for the middle **Y123** based DSC.

Table S5. Summary of SSM DSC device performance, as given in Figure S7.

Cell type*	Position	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF %	PCE %
D35/Y123/AP25+D35	SSM-DSCs	2391	5.3	67	8.5
D35/Y123/AP25+D35	SSM-DSCs with a 400 mm filter	2370	4.7	74	8.1

* Device details are the same as in Table S3.

Table S6. Comparison of water electrolysis parameters at two times.

Experiment Number		Time (h)	V_{oc} (V)	J_{op} (mA cm^{-2})	*FE*	Solar-to-H$_2$ (STH) efficiency (%)
1		1	1.23	3.77	0.82	3.8
2		1	1.23	3.72	0.86	3.9
2		4	1.23	3.65	0.78	3.5

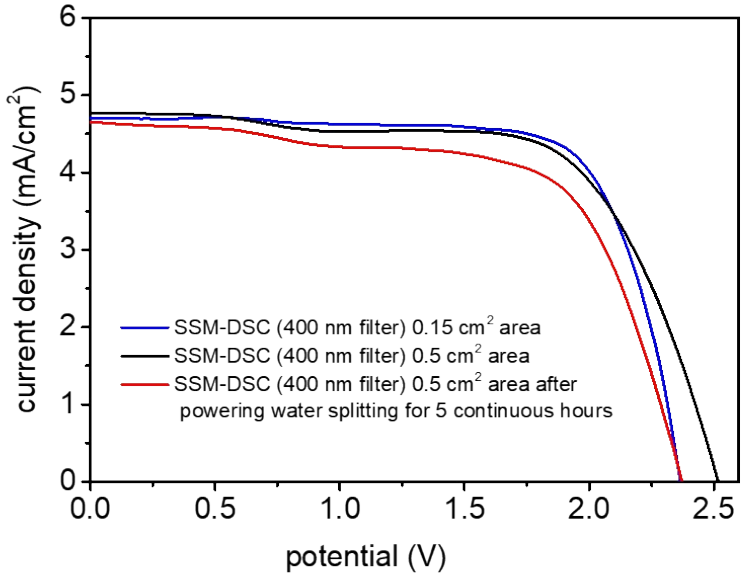

Figure S8. *J-V* curves summarizing the effect of illuminated area change and stability after powering water splitting for continuous 5 h.

Table S7. Summary of SSM-DSC device performance parameters before and after powering the water splitting system for 5 h.

Dye (TiO$_2$ thickness)/Redox Shuttle	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF %	PCE %
D35 (1.5 µm)/Co(bpy-pz)$_2^{3+/2+}$	989	4.8	70	3.4
Y123 (3.0 µm)/Co(bpy)$_3^{3+/2+}$	790	4.6	75	2.8
AP25+D35 (15 µm)/(I$^-$/I$_3^-$)	581	4.9	79	2.3
D35/Y123/AP25+D35	2521	4.8	70	8.1
After 5 h continuous irradiation for H$_2$O splitting				
D35 (1.5 µm)/Co(bpy-pz)$_2^{3+/2+}$	922	5.3	65	3.2
Y123 (3.0 µm)/Co(bpy)$_3^{3+/2+}$	756	5.4	70	2.9
AP25+D35 (15 µm)/(I$^-$/I$_3^-$)	578	5.0	79	2.4
D35/Y123/AP25+D35	2364	4.7	64	7.4

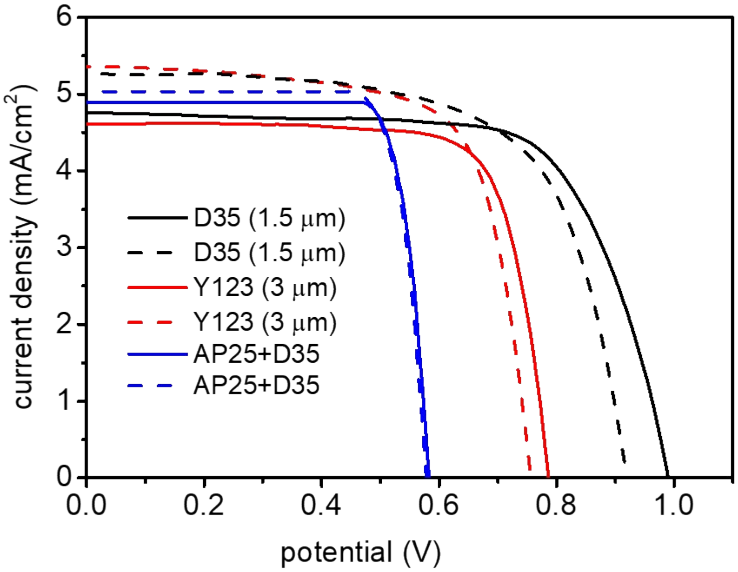

Figure S9. *J-V* curves of 1st, 2nd, and 3rd subcell in the SSM-DSCs before (solid line) and after (dash line) powering the water splitting system continuously for 5 h with a 400 nm filter attached.

5. NanoCOT fabrication

NanoCOT was fabricated by converting Ti nanowires (NW) to TiO_2 followed by chemical vapor deposition (CVD) process. Briefly, Ti NWs substrates were prepared using a hydrothermal reaction process by 99% purity Ti plates in a Teflon-lined stainless steel autoclave containing 0.6 M HCl solution and heated at 190 °C for 12 h. After cooling to room temperature, the as-prepared Ti NWs substrates were thoroughly washed with distilled water and dried in air. Subsequently, the samples were annealed at 450 °C for 2 h (in air) and allowed to cool to room temperature to form a thin TiO_2 layer on the Ti NWs substrate. The thermally annealed TiO_2 NWs substrates were loaded with $Fe(NO_3)_3$ before placing them horizontally into a quartz boat. The boat is covered with a quartz plate on top to allow sufficient mixture gas retention time to complete the carbon transformation reaction. The boat was loaded in a tube furnace filled and purged with a pure N_2 stream to thoroughly remove oxygen. The furnace temperature was set to 900 °C with a ramp rate of 50 °C/min and a dwell time of 1 h. At ~600 °C, the N_2 gas was turned off, and the $CH_4/H_2/N_2$ gas mixture was turned on at a flow rate of ~1000 sccm and reduced to ~100 sccm when the temperature reached 800 °C. After the carbon transformation reaction, the furnace was allowed to cool under $CH_4/H_2/N_2$ flow until the temperature of the furnace reached ~600 °C. At this temperature, the $CH_4/H_2/N_2$ was turned off, and the N_2 flow was turned back on. The samples were allowed to cool to room temperature in an N_2 stream before being removed from the furnace.

6. Electrodeposition of NiMoZn/NanoCOT Cathode

NiMoZn alloy was electrodeposited onto a fresh-made NanoCOT electrode in a three-electrode configuration. The plating solution is comprised of nickel (II) chloride hexahydrate (9.51 g L^{-1}), sodium molybdate dihydrate (4.84 g L^{-1}), anhydrous zinc chloride (0.0409 g L^{-1}), tetrabasic sodium pyrophosphate (34.57 g L^{-1}), and sodium bicarbonate (74.77 g L^{-1}). Hydrazine hydrate (1.21 mL L^{-1}) was added immediately into the plating solution before plating. The NiMoZn alloy was deposited onto the NanoCOT electrode at a potential of −1.5 V vs. Ag/AgCl for 20 min. The obtained electrodeposited film was then stored in 10 M KOH for 16 h to activate its surface by obtaining a suitable stoichiometry for an enhanced HER.

7. Crude Cost Analysis

Table S8. Crude cost analysis for key raw materials to build a PV-EC system using precious metals versus a precious metal free system using the components reported in Figure 1 of the main text.

Precious Metal or Precious Metal Free System	**Material Used**	**Price**
Counter Electrode Material		
Precious Metal System	H_2PtCl_6	$126/gram
Precious Metal Free System	GNP	$10/gram
Dyes		
Precious Metal System	B11 (thiophene)	$0.20/gram
Precious Metal System	B11 (1-bromohexane)	$0.20/gram
Precious Metal System	B11 ($ClSnMe_3$)	$8/gram
Precious Metal System	B11 (2-bromothiophene)	$1.5/gram
Precious Metal System	B11 (4,4'-dibromo-2,2'-bipyridine)	$55/gram

Precious Metal System	B11 ([$RuCl_2$(p-cymene)]$_2$)	$60/gram
Precious Metal System	B11 (NH_4NCS)	$0.50/gram
Precious Metal System	B11 (total raw materials cost)	~$125/gram
Precious Metal Free System	AP25 (3,4-dibromothiophene)	$14/gram
Precious Metal Free System	AP25 (thioglycene)	$0.30/gram
Precious Metal Free System	AP25 (CPDT)	$70/gram
Precious Metal Free System	AP25 (1-bromo-2-ethylhexane)	$0.4/gram
Precious Metal Free System	AP25 ($SnBu_3Cl$)	$0.6/gram
Precious Metal Free System	AP25 (1-bromohexane)	$0.2/gram
Precious Metal Free System	AP25 (4-iodophenol)	$3/gram
Precious Metal Free System	AP25 (4-bromoanaline)	$0.7/gram
Precious Metal Free System	AP25 (B_2pin_2)	$8/gram
Precious Metal Free System	AP25 (cyanoacetic acid)	$0.2/gram
Precious Metal Free System	AP25 (total raw material cost)	~$97/gram
Precious Metal Free System	Y123 (CPDT)	$70/gram
Precious Metal System	Y123 (1-bromohexane)	$0.20/gram
Precious Metal System	Y123 (bis(4-bromophenyl)amine)	$8/gram
Precious Metal System	Y123 (4-bromoresorcinol)	$7/gram
Precious Metal Free System	Y123 ($SnBu_3Cl$)	$0.6/gram
Precious Metal Free System	Y123 (cyanoacetic acid)	$0.2/gram
Precious Metal Free System	Y123 (total raw material cost)	~$86/gram
Electrode Material Costs		
Precious Metal System	H_2IrCl_6	$200/gram
Precious Metal System	Titanium Substrate	$0.8/gram
Precious Metal Free System	NanoCOT: Titanium Foil	$0.8/gram
Precious Metal System	Pt	$400/gram
Precious Metal Free System	NiMoZn: Titanium Foil	$0.8/gram
Precious Metal Free System	NiMoZn: $NiCl_2$*$6H_2O$	$0.6/gram
Precious Metal Free System	NiMoZn: Na_2MoO_4	$0.8/gram
Precious Metal Free System	NiMoZn: ZnCl	$0.7/gram
Precious Metal Free System	NiMoZn: Hydrazine	$0.3/gram
Precious Metal System	Electrode Total Cost	$600/gram
Precious Metal Free System	Electrode Total Cost	$4/gram

We stress that this is a very crude analysis of only raw material costs without adjusting to product yields, bulk purchasing price adjustments, solvents, common reagents, atom economy, relative amounts of materials needed, etc. Reagents readily available at <\$0.1/gram are not included in the list above.

Table S9. Crude cost analysis of full PV-EC systems using sums from Table S8 above.

Precious Metal or Precious Metal Free System	**Component**	**Price**
Precious Metal System	3 Solar Cell Counter Electrodes (at \$126/gram of raw material each)	~\$375
Precious Metal System	2 Sensitized Electrodes with **B11** (at \$125/gram of raw material each)	\$250
Precious Metal System	Electrocatalysts	\$600
Precious Metal System	**PV-EC System**	**\$1225**
Precious Metal Free System	2 Solar Cell Counter Electrodes (GNP at \$10/gram of raw material each)	\$20
Precious Metal Free System	2 Sensitized Electrodes (1 with **Y123**, 1 with **AP25**)	\$183
Precious Metal Free System	Electrocatalysts	\$4
Precious Metal Free System	**PV-EC System**	**\$207**

8. References

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