

Electronic Supplementary Information

A Low Recombination Indolizine Sensitizer for Dye-Sensitized Solar Cells

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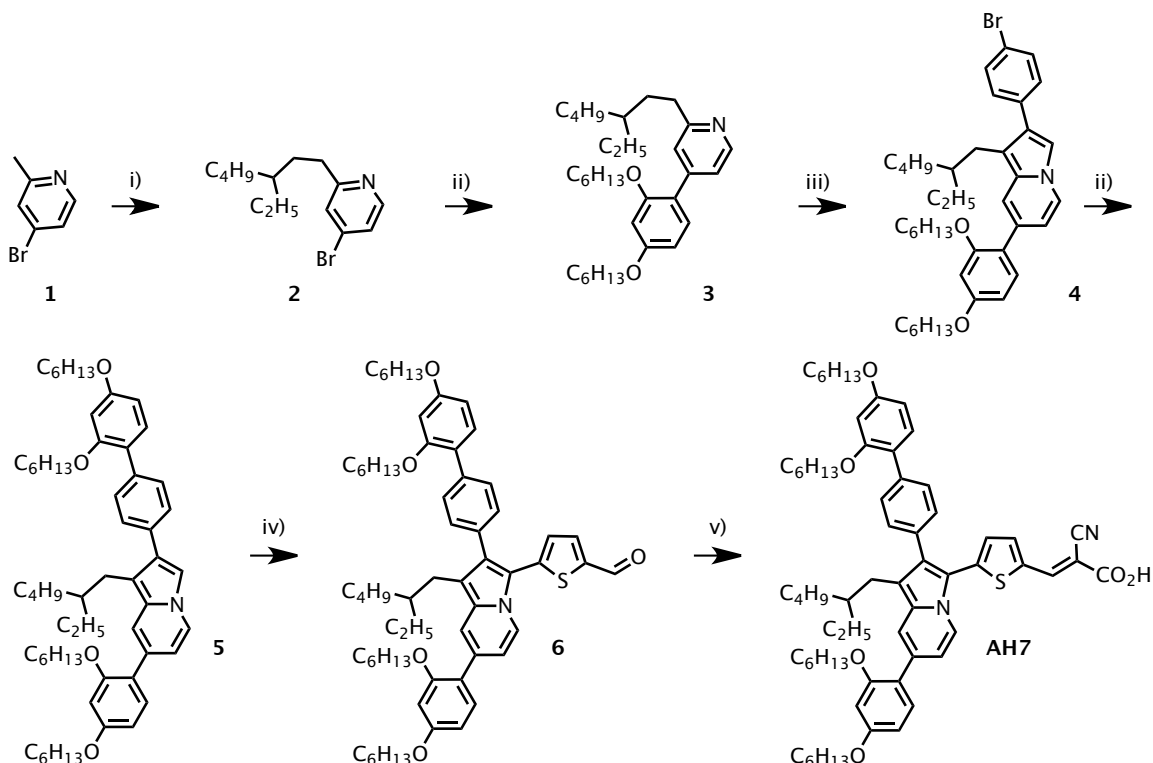
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Synthetic Information



Scheme S1. Synthetic route to **AH7**. *Conditions:* i): LDA, THF, 2-ethylhexyliodide, -78°C , 69%. ii): 2,4-bis(hexyloxy)phenylboronic acid, $\text{Pd}(\text{PPh}_3)_4$, Aliquat 336, Na_2CO_3 , H_2O , toluene, reflux, **3**: 69%, **5**: 88%. iii): a) 2,4'-dibromoacetophenone, acetone, reflux, b) NaHCO_3 , H_2O , reflux, 79%. iv): 5-bromo-2-thiophenecarboxaldehyde, $\text{PdCl}_2(\text{PPh}_3)_2$, KOAc, NMP, 80°C , 81%. v): $\text{NCCH}_2\text{CO}_2\text{H}$, piperidine, CHCl_3 , 90°C , 82%.

General Information: All commercially obtained reagents were used as received. Thin-layer chromatography (TLC) was conducted with Sigma T-6145 precoated TLC silica gel 60 (F254) polyester sheets and visualized with UV and potassium permanganate staining. Flash column chromatography was performed with Sorbent Tech P60, 40–63 μm (230–400 mesh). ^1H NMR spectra were recorded on a Bruker Avance-300 (300 MHz), Bruker Avance DRX-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, b = broad, ap = apparent; coupling constant(s) in Hz; integration. UV–Vis spectra were measured with a Cary 5000 UV–Vis spectrometer. Cyclic voltammograms were measured with a C-H Instruments electrochemical analyzer.

Synthetic Procedures:

2-(3-ethylheptyl)-4-bromopyridine (2): A flame dried flask was charged with dry, degassed THF (9 mL) and diisopropylamine (2.38 mL, 16.9 mmol) was added and cooled to -78°C . Once cool, n-butyl lithium (2.5 M, 6.8 mL) was added dropwise via syringe. After 15 minutes, the LDA solution was transferred via cannula to a flame dried flask

equipped with a stirbar that had previously been charged with hexane (4 mL) and 4-bromo-2-picoline **1** (1.81 mL, 15.4 mmol). After 45 minutes at -78°C , ethylhexyliodide (3.7 g, 15.4 mmol) was added dropwise via syringe, the solution was kept at -78°C overnight and warmed to r.t. the following morning. The reaction mixture was poured into ice water then diluted with DCM (100 mL) and washed with H_2O (3 x 50 mL). The crude material was passed through SiO_2 plug using first hexanes, then 10% EA:Hx. Product fractions were concentrated to yield a pale yellow oil (3.00 g, 69%). ^1H NMR (500 MHz, CDCl_3) δ 8.33 (d, $J = 5.5$ Hz, 1H), 7.33 (d, $J = 2$ Hz, 1H), 7.26 (dd, $J = 2$ Hz, 5.5 Hz, 1H), 2.73 (t, $J = 8$ Hz, 2H), 1.65 (m, 2H), 1.37-1.24 (m, 10H), 0.89 (t, $J = 7$ Hz, 3H), 0.87 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (300 MHz, CDCl_3) δ 164.9, 150.3, 133.2, 126.2, 124.5, 39.0, 35.9, 33.6, 33.0, 29.2, 26.1, 23.4, 14.5, 14.4, 11.1. IR (neat): 3458 (br), 2958, 2925, 2857, 1648. HRMS m/z calculated for $\text{C}_{14}\text{H}_{22}\text{BrN}$ $[\text{M}+\text{H}]^+$: 284.1014, found 284.0929.

2-(3-ethylheptyl)-4-(2,4-bis(hexyloxy)phenyl)pyridine (3): A flask equipped with reflux condenser and stirbar was charged with **2** (1.95 g, 6.86 mmol), 2,4-bis(hexyloxy)phenylboronic acid (2.66 g, 8.23 mmol) and dissolved in 6:1 Toluene : 2M Na_2CO_3 (aq) (34 mL total). Aliquat 336 (3 drops) was added and the solution bubbled vigorously with N_2 . After 30 min, $\text{Pd}(\text{PPh}_3)_4$ (0.31 g, 0.27 mmol) added in one solid portion from a vial, the reaction mixture was heated to Toluene reflux, allowed to stir, and was monitored by ^1H NMR spectroscopy. After 18h, reaction mixture was cooled to r.t., the organic layer was separated and the crude reaction mixture loaded directly onto SiO_2 plug. The mixture was passed through with Hexanes (250 mL), then 5%EtOAc:Hexanes (250 mL), then 10%EtOAc:Hexanes (500 mL), then 25%EtOAc:Hexanes (500 mL) through plug. Product fractions were concentrated to yield a mixture of product and protodeboronated starting material (2.28g, 69% yield, 3.30 g of a 67% impure mixture). Used without further purification. ^1H NMR (300 MHz, CDCl_3) δ 8.5 (d, $J = 5.4$ Hz, 1H), 7.34 (s, 1H), 7.26 (m, 2H), 6.59 (ap s, 1H), 6.56 (s, 1H), 3.99 (m, 4H), 2.8 (m, 2H), 1.85-1.74 (m, 6H), 1.5-1.3 (m, 22 H), 0.96-0.87 (m, 12 H). ^{13}C NMR (300 MHz, CDCl_3) δ 164.6, 149.9, 132.9, 125.9, 124.2, 38.7, 35.6, 33.3, 32.7, 28.8, 25.7, 23.1, 14.1, 10.8. IR (neat): 3060 (br), 2958, 2931, 2870, 1611. HRMS m/z calculated for $\text{C}_{32}\text{H}_{51}\text{NO}_2$ $[\text{M}+\text{H}]^+$: 482.3998, found 482.3402.

2-(4-bromophenyl)-3-(2-ethylhexyl)-5-(2,4-bis(hexyloxy)phenyl)indolizine (4): A flask equipped with a reflux condenser and stirbar was charged with **3** (2.60 g, 5.4 mmol), 2,4'-dibromoacetophenone (1.50 g, 5.4 mmol), dissolved in acetone (25 mL), set to stir, heated to reflux, and monitored by ^1H NMR spectroscopy. After 15h, the reaction mixture was cooled to rt, concentrated, and suspended in degassed H_2O (20mL). NaHCO_3 was added (1.81 g, 21.6 mmol), and the reaction mixture was set to stir, heated to reflux, and monitored by ^1H NMR spectroscopy. After 2h, CH_2Cl_2 (50 mL) was added, org. layer separated and diluted with Hexanes (200 mL), passed through a short plug of SiO_2 using first with 25% CH_2Cl_2 :Hexanes (500 mL), then DCM (1.5L). Concentrated product fractions to yield an off-white solid (2.83 g, 79%). ^1H NMR (300 MHz, CDCl_3) δ 7.80 (d, $J = 6.6$ Hz, 1H), 7.51 (d, $J = 8.4$ Hz, 2H), 7.45 (s, 1H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.27 (s, 2H), 6.71 (dd, $J = 1.8$ Hz, 4.2 Hz, 1H), 6.55 (m, 2H), 6.46 (ap d, $J = 8.0$ Hz, 1H), 3.95 (m, 4H), 2.77 (m, 2H), 1.83-1.72 (m, 6 H), 1.5-1.24 (m, 22 H), 0.96-0.87 (m, 12 H).

2-(4-(2,4-bis(hexyloxy)phenyl)-3-(2-ethylhexyl)-5-(2,4-bis(hexyloxy)phenyl)indolizine (**5**): A flask equipped with reflux condenser and stirbar was charged with **4** (2.83 g, 4.28 mmol), 2,4-bis(hexyloxy)phenylboronic acid (1.66 g, 5.14 mmol) and dissolved in 6:1 Toluene : 2M Na₂CO₃ (aq) (23 mL total). Aliquat 336 (3 drops) was added and the solution bubbled vigorously with N₂. After 30 min, Pd(PPh₃)₄ (0.20 g, 0.17 mmol) was added in one solid portion from a vial, the reaction mixture was heated to Toluene reflux, allowed to stir, and was monitored by ¹H NMR spectroscopy. After 2h, reaction mixture cooled to rt, the org. layer separated and directly subjected to column chromatography using 350 mL SiO₂, 25% CH₂Cl₂:Hexanes, product spot concentrated to yield a pale yellow solid (3.30 g, 88%). ¹H NMR (300 MHz, CDCl₃) δ 7.82 (d, J = 7.2 Hz, 1H), 7.59 (d, J = 9 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.46 (s, 1H), 7.33 (s, 1H), 7.29 (dd, J = 1.8 Hz, 9 Hz), 6.69 (dd, J = 3 Hz, 7.5 Hz, 1H), 6.56 (m, 4H), 3.98 (m, 8H), 2.84 (ap d, J = 7.2 Hz, 2H), 1.89-1.7 (m, 10H), 1.55-1.2 (m, 34 H), 0.96-0.87 (m, 18 H). ¹³C NMR (500 MHz, CDCl₃) δ 159.7, 159.6, 157.2, 157.1, 136.3, 134.5, 131.5, 131.1, 130.4, 129.8, 129.3, 128.3, 126.3, 123.5 (2C), 122.7, 116.9, 112.7, 110.7, 109.9, 105.4, 105.3, 100.6, 100.5, 68.5, 68.4, 68.2, 68.1, 53.4, 40.7, 34.7, 34.5, 32.7, 31.6, 31.5, 31.5, 29.3, 29.3, 29.2, 29.1, 29.1, 28.7, 28.7, 25.8, 25.8, 25.3, 23.1, 22.6, 22.6, 20.7, 14.1 (2C), 14.0, 14.0, 11.4, 10.9. IR (neat): 3455 (br), 2955, 2931, 1699, 1652. HRMS *m/z* calculated for C₅₈H₈₃NO₄ [M+H]⁺: 858.6400, found 858.6425.

1-(thiophen-2'-yl-5'-carboxaldehyde)-2-(4-(2,4-bis(hexyloxy)phenyl)-3-(2-ethylhexyl)-5-(2,4-bis(hexyloxy)phenyl)indolizine (**6**): To an amber vial equipped with a stirbar was added 2-bromo-5-thiophenecarboxaldehyde (0.019 mL, 0.165 mmol), **5** (0.10 g, 0.11 mmol), NMP (1 mL). After degassing with N₂ for 30 min, PdCl₂(PPh₃)₂ (0.0039 g, 0.0055 mmol), KOAc (0.016 g, 0.165 mmol) were added in one solid portion. The reaction mixture was heated to 80°C, allowed to stir, and monitored by ¹H NMR spectroscopy. After 5 h, the reaction mixture was directly subjected to column chromatography using solvent gradient of hexanes to 3% EtOAc:hexanes to 5% acetone:hexanes. Product spot concentrated to yield a red oil (0.086g, 81%). ¹H NMR (300 MHz, CDCl₃) δ 9.79 (s, 1H), 8.53 (d, J = 7.5 Hz, 1H), 7.58 (apd, J = 4.2 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.31 (m, 2H), 7.23 (2, 1H), 6.9 (m, 2H), 6.58 (m, 4H), 3.99 (m, 8H), 2.66 (apd, J = 5.4, 2H), 1.86-1.55 (m, 10H), 1.5-1.05 (m, 33 H), 0.95-0.6 (m, 18 H). ¹³C NMR (300 MHz, CDCl₃) δ 182.2, 160.1, 159.8, 157.3, 157.1, 143.8, 140.1, 137.4, 136.7, 133.6, 133.1, 132.4, 131.1, 130.4, 130.0, 129.4, 129.0, 126.4, 123.3, 121.9, 121.7, 117.0, 114.8, 114.6, 114.4, 105.6, 105.4, 100.5 (2C), 68.6, 68.3, 68.2, 68.1, 53.4, 40.7, 32.7, 31.6, 31.5 (3C), 29.7, 29.3 (2C), 29.1, 28.7, 28.3, 25.8 (4C), 23.0, 22.6 (4C), 14.0 (4C), 10.8, 1.0. IR (neat): 3029 (br), 2955, 2928, 2857, 1667. HRMS *m/z* calculated for C₆₃H₈₅NO₅S [M+Cs]⁺: 1100.5203, found 1100.4452.

3-(thiophen-2'-yl-5'-carboxaldehyde)-2-(4-(2,4-bis(hexyloxy)phenyl)-3-(2-ethylhexyl)-5-(2,4-bis(hexyloxy)phenyl)indolizine)-2-cyano-2-propenoic acid (**AH7**). A flask equipped with a stirbar was charged with **6** (0.043 g, 0.044 mmol), CHCl₃ (0.85 mL) and degassed with N₂. After 30 min, cyanoacetic acid (0.011 g, 0.13 mmol) and piperidine (0.039 mL, 0.31 mmol) added and the flask sealed with a plastic stopper and electrical tape. The reaction mixture was heated to 90°C with stirring and was monitored by TLC.

After 1.5 hours, the reaction mixture was cooled to rt, and the mixture was poured onto a pad of SiO₂ wetted with DCM. DCM was passed until the orange band passed, then 50% MeOH:DCM was used to elute the product. The MeOH:DCM solution was evaporated, hexanes was added (100 mL) and H₂O (50 mL) was added for a single, rapid extraction. Extended exposure to water results in a color change likely due to a retro-Knoevenagel condensation. The hexanes layer was directly evaporated and gave the product as a black solid without need of further purification (0.038 g, 82%). ¹H NMR (300 MHz, CDCl₃) δ 9.79 (s, 1H), 8.53 (d, J = 7.5 Hz, 1H), 7.58 (ap d, J = 4.2 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.31 (m, 2H), 7.23 (2, 1H), 6.9 (m, 2H), 6.58 (m, 4H), 3.99 (m, 8H), 2.66 (ap d, J = 5.4, 2H), 1.86-1.55 (m, 10H), 1.5-1.05 (m, 34 H), 0.95-0.6 (m, 18 H). IR (neat): 2920, 2852.

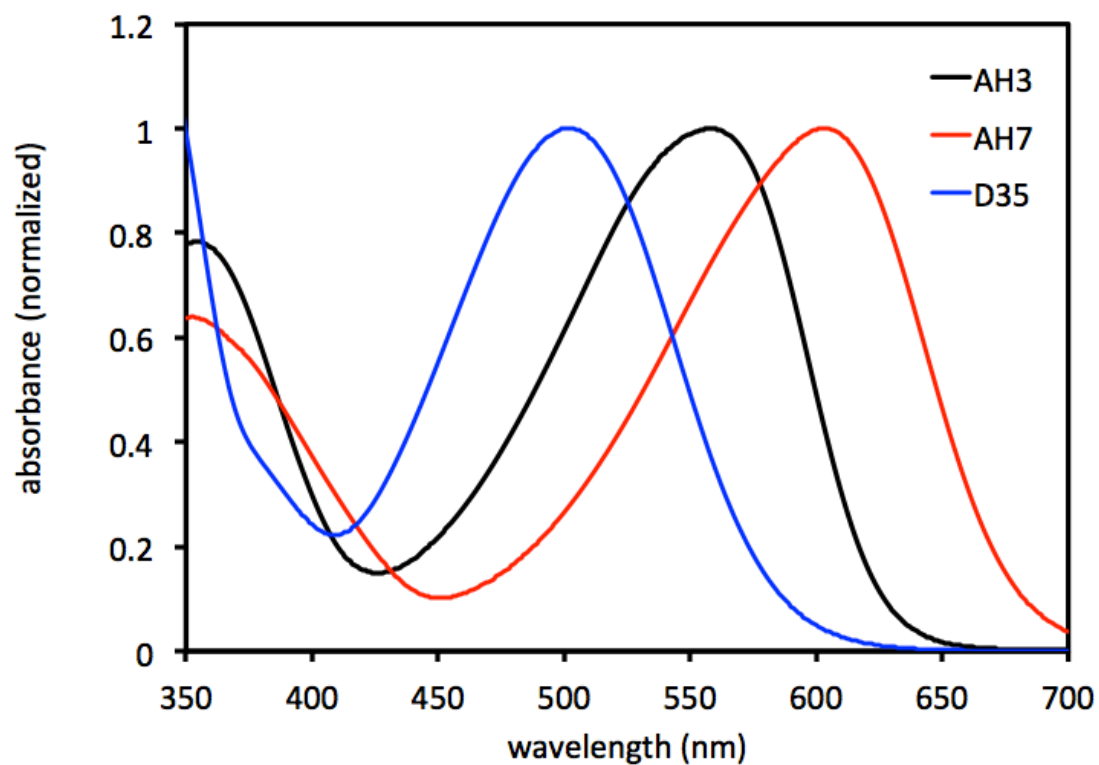
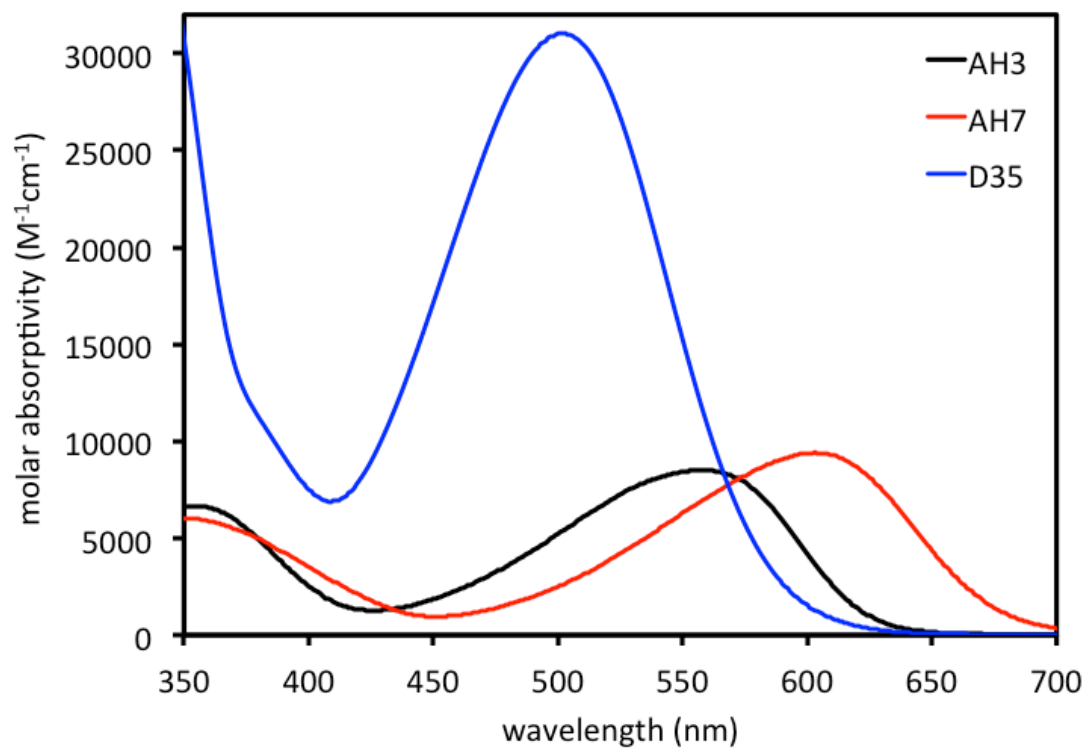


Figure S1. Absorption spectrum comparison of AH3, AH7 and D35 as a molar absorptivity plot (top) and as a normalized plot (bottom).

Photovoltaic Characterization: A 450W xenon lamp (Oriel, USA) was used as a light source to study the current–voltage characteristics of the DSC. The spectral output of the lamp was filtered using a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) to reduce the mismatch between the simulated and actual solar spectrum to less than 2%. The Keithley model 2400 digital source meter (Keithley, USA) was used for data acquisition. The photoactive area of 0.16 cm² was defined by a black mask of 4x4 mm². Incident photon-to-current conversion efficiency measurements were carried from the monochromated visible photons, from Gemini-180 double monochromator Jobin Yvon Ltd. (UK), powered by a 300 W xenon light source (ILC Technology, USA) superimposed on a 10 mW cm⁻² LED light. The monochromatic incident light was passed through a chopper running at 2 Hz frequency and the on/off ratio was measured by an operational amplifier.

Device Fabrication: For the photoanode, TEC 15 glass 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 and sonicated in acetone 10 minutes followed by sonication in ethanol for 10 minutes. Finally the electrodes were placed under UV/ozone for 15 minutes (UV-Ozone Cleaning System, Model ProCleaner by UVFAB Systems). A compact TiO₂ underlayer is then applied by pretreatment of the substrate submerged in a 40 mM TiCl₄ solution in water (prepared from a 2M TiCl₄ stock solution kept in the freezer). The submerged substrates (FTO up) were heated for 30 minutes at 70 °C. After heating, the substrates were rinsed first with water then with ethanol. *For cobalt based cells:* The photoanode consists of thin TiO₂ electrodes comprised of a 5.5 μm mesoporous TiO₂ layer (particle size, 30 nm, Dyenamo DN-GPS-30TS, 2 prints) screen printed from a Sefar screen (90/230–48W) and a 5.0 μm TiO₂ scattering layer (particle size, 400 nm, CCIC, 1 print) screen printed from a Sefar screen (54/137–64W). *For iodine based cells:* The photoanode consists of thin TiO₂ electrodes comprising a 9.5 μm mesoporous TiO₂ layer (particle size, 20 nm, Dyesol, DSL 18NR-T, 2 prints) and a 5.0 μm TiO₂ scattering layer (particle size, 400 nm, CCIC, 1 print). Both layers were screen printed from a Sefar screen (54/137–64W). Between each print, the substrate was heated for 7 minutes at 125°C and the thickness was measured with a profilometer. Film thicknesses were measured with an Alpha-Step D-500 KLA Tencor profilometer. The substrate was then sintered with progressive heating from 125°C (5 minute ramp from r.t., 5 minute hold) to 325 °C (15 minute ramp from 125°C, 5 minute hold) to 375 °C (5 minute ramp from 325 °C, 5 minute hold) to 450 °C (5 minute ramp from 375 °C, 15 minute hold) to 500 °C (5 minute ramp from 450 °C, 15 minute hold). The cooled sintered photoanode was soaked 30 min at 70 °C in a 40 mM TiCl₄ water solution and heated again at 500 °C prior to sensitization. The complete working electrode was prepared by immersing the TiO₂ film into the dye solution for 2 hours (cobalt) or 5 hours (iodide). The solution is 0.2 mM of dye in THF:ethanol mixture (1:4). The dye:CDCA molar ratio for the optimized device is 1:40. A thermally platinized fluorine-doped tin oxide (FTO, TEC 7 Hartford Glass) glass counter electrode by placing 1-2 drops of 0.1 M H₂PtCl₄ in *i*-PrOH so the entire FTO surface is covered. The solution was dried then a heat gun was used to warm the substrates at 410 °C for 20 minutes. After allow them to cool to room temperature, the working electrodes were then sealed with a 25 μm thick hot melt film (Surlyn, Dupont)

by heating the system at 100 °C. Devices were completed by filling the electrolyte by pre-drilled holes in the counter electrodes and finally the holes were sealed with a Surlyn sheet and a thin glass cover by heating. A black mask (4x4 mm²) was used in the subsequent photovoltaic studies.

Attempts to determine surface coverage of **AH7** and **AH3** through typical desorption methods utilizing Bu₄NOH/DMF as well as dilute acid solutions led to dye decomposition for the **AH** dyes in these solutions.

Dye Loading: TEC 15 glass was cut into 2x2 cm squares and sonicated sequentially at room temperature in 0.2% aqueous Deconex 21 (15 minutes), acetone (10 minutes), and finally ethanol (10 minutes). TiO₂ films were comprised of a 3 μm TiO₂ layer (particle size, 20 nm, Dyesol, DSL 18NR-T, 1 print) printed from a Sefar screen (90/230-48W). Films were heated at 125 °C for 7 minutes. Films were then sintered with progressive heating from 125 °C (5 minute ramp from r.t., 5 minute hold) to 325 °C (15 minute ramp from 125 °C, 5 minute hold) to 375 °C (5 minute ramp from 325 °C, 5 minute hold) to 450 °C (5 minute ramp from 375 °C, 15 minute hold) to 500 °C (5 minute ramp from 450 °C, 15 minute hold). Upon cooling to room temperature, films were submerged for 5 hours in a 0.2 mM dye solution in THF:EtOH (1:4). The dye:CDCA molar ratio was 1:40 as in optimized devices. Absorbance measurements were taken for TiO₂ films sensitized with **AH3**, **AH7**, and **D35** (**Figure S2, top**). **D35** films were submerged in 5 mL of 0.01 M Bu₄NOH/DMF for 1 hour at room temperature. Complete desorption of the dye from the TiO₂ was confirmed by a lack of color in the film. The amount of **D35** on the TiO₂ surface was calculated using Beer's Law ($A = \epsilon lc$) where the molar absorptivity of **D35** in 0.01 M Bu₄NOH/DMF was independently measured to be 41,000 M⁻¹cm⁻¹. Due to instability of **AH3** and **AH7** in basic DMF solution, loadings were derived by assuming relative molar absorptivity ratios between **AH3/D35** and **AH7/D35** were roughly similar in DCM solutions and on TiO₂ films. Absorbances were divided by these ratios to give a normalized absorbance curve for each dye (**Figure S2, bottom**). The ratio of peak absorbance values of **AH3/D35** and **AH7/D35** in the normalized curve were used to determine the molar amount of each **AH** dye by comparing to the known amount of **D35** found through desorption studies. The dye loading amounts listed in Table S1 are corrected to match the film thickness used in devices (10 μm) as the film absorbances require a thinner film than is used in optimal devices.

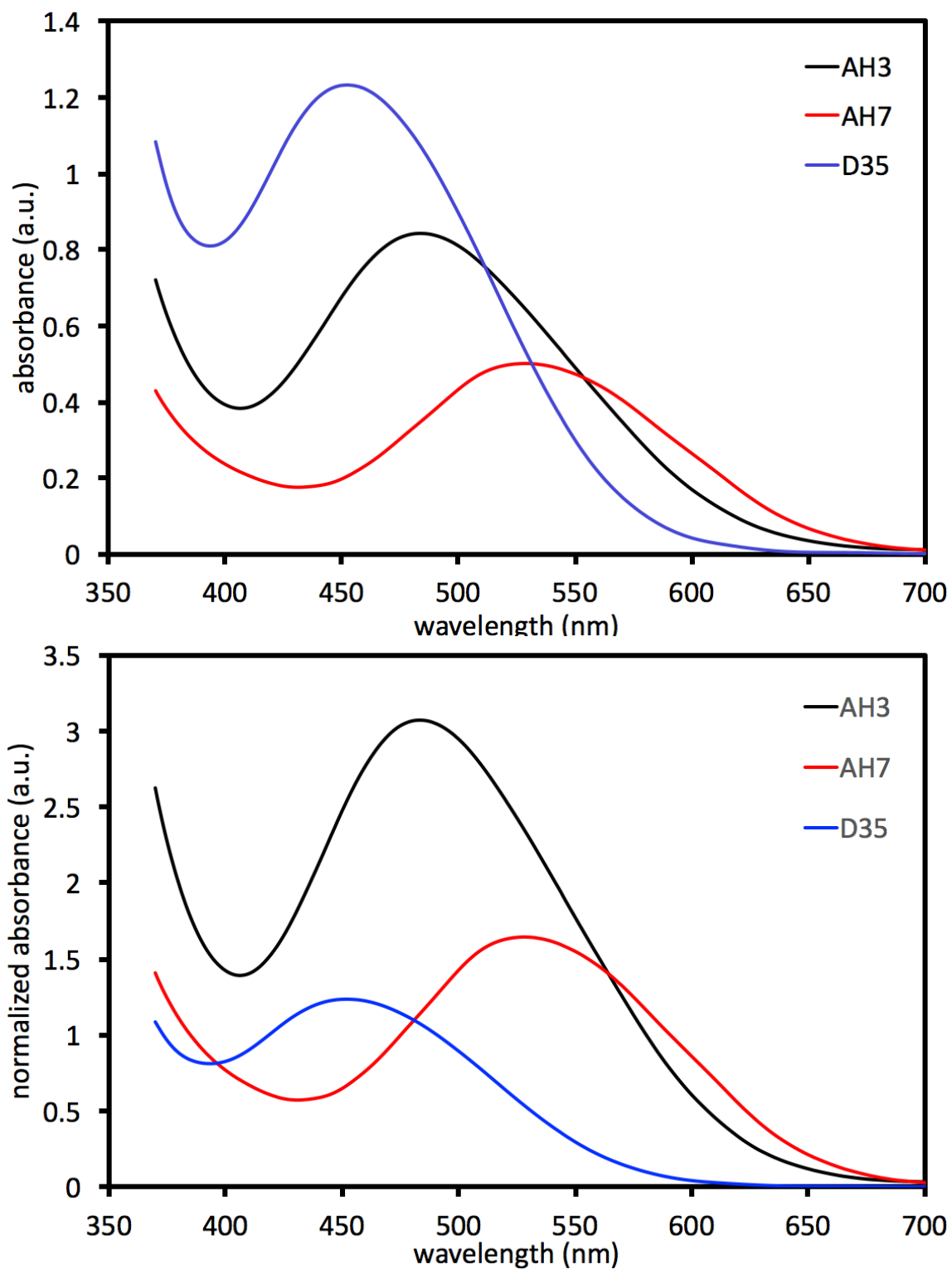


Figure S2. Absorbance spectra of AH3, AH7, and D35 on TiO₂ films (top). Absorbance spectra of AH3, AH7, and D35 on TiO₂ derived from the molar absorptivity ratios of AH3/D35 and AH7/D35 in DCM solutions (bottom).

Dye	λ_{\max} (nm)	λ_{onset} (nm)	Dye Loading ($\times 10^{-4}$ mol/cm ²)
AH3	483	620	3.57
AH7	528	660	1.91
D35	452	570	1.43

TiO₂ Conduction Band Analysis:

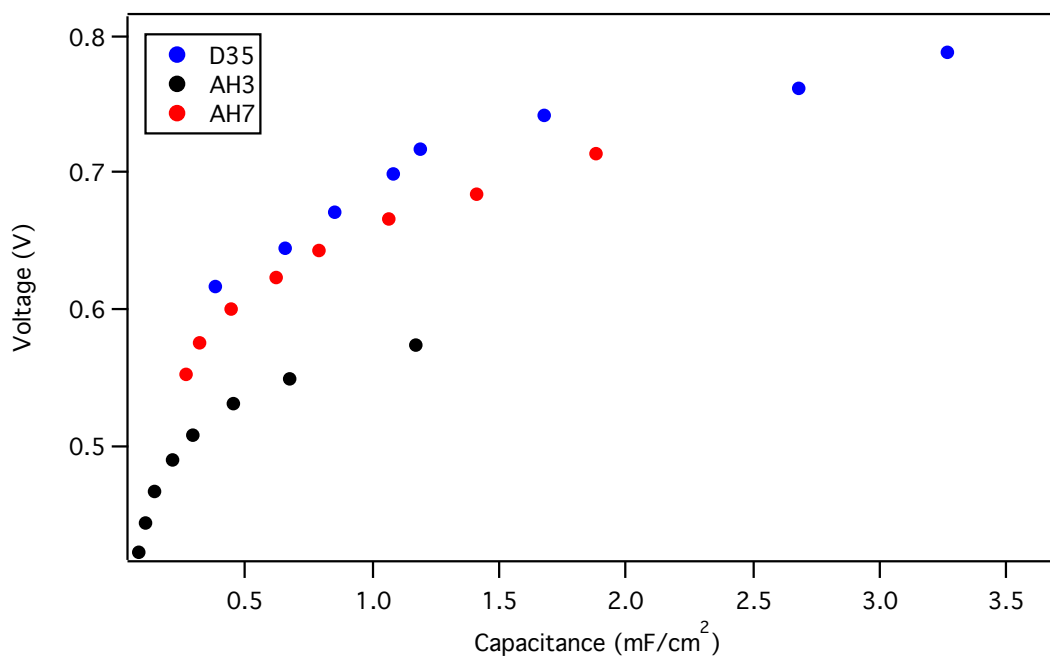


Figure S3. Plot of TiO₂ chemical capacitance versus voltage for films sensitized with dyes **AH3**, **AH7**, and **D35**.