colorants

Supplementary Materials

Mathematical Approach to Optimizing the Panchromatic Absorption of Natural Dye Combinations for Dye-Sensitized Solar Cells

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Dye Extraction Procedures

Prickly Pear fruits were harvested in the foothills of Albuquerque, New Mexico, while the Aroniaberries, Turmeric, Spinach, Mangosteen Pericarp and Blue Spirulina were purchased online. Reference Figure 1 for a photo of the organic precursor materials. Dyes were extracted into ice-cold reagent grade Methanol via mechanical lysis using a mortar and pestle [1]. A fixed mass of 6g of organic material per 100 mL of solvent was used in all cases. Agitation of the organic material in the solvent was performed for 10 minutes until a dark saturated solution was obtained. Anhydrous Na_2SO_4 desiccant was then added to remove any trace amounts of water. The solutions were then vacuum filtered through 40 µm paper to remove the remaining organic material and desiccant. The pH of the Anthocyanin and Phycocyanin solutions was adjusted to 3.0 and 5.5 respectively using HNO_3 while the remaining solutions were kept at pH 7.0 [2]. All dye extracts were then capped and stored in a cold, dark refrigerator to limit dye degradation [1]. The purity of these dye extracts was analyzed qualitatively by first cooling the solutions to near the solvent melting temperature and centrifuging at 20,000 RCF for two hours to pellet any co-extracts with marginal solubility. No such pelleting was observed during these experiments nor did any cloudiness appear. Furthermore, gel electrophoresis was performed to assess the presence of DNA impurities which exhibit somewhat high MeOH solubility [3]. Only very marginal banding occurred in the Anthocyanin samples at ~5500 bp.

Figure S1. Precursor materials used for dye extractions. Reference Figure 2 of the main manuscript for a photo of the final dye extracts.

Generation of Dye Combinations

The list of dye combinations produced in this work (including the individual dyes) were: A, B, K, M, C, P, AB, AK, AM, AC, AP, BK, BM, BC, BP, KM, KC, KP, MC, MP, CP, ABK, ABM, ABC, ABP, AKM, AKC, AKP, AMC, AMP, ACP, BKM, BKC, BKP, BMC, BMP, BCP, KMC, KMP, KCP, MCP and ABKMCP. A photo of the final dye combinations is shown in Figure 2.

Row 1
Row 2
Row 3
Row 4
Row 5

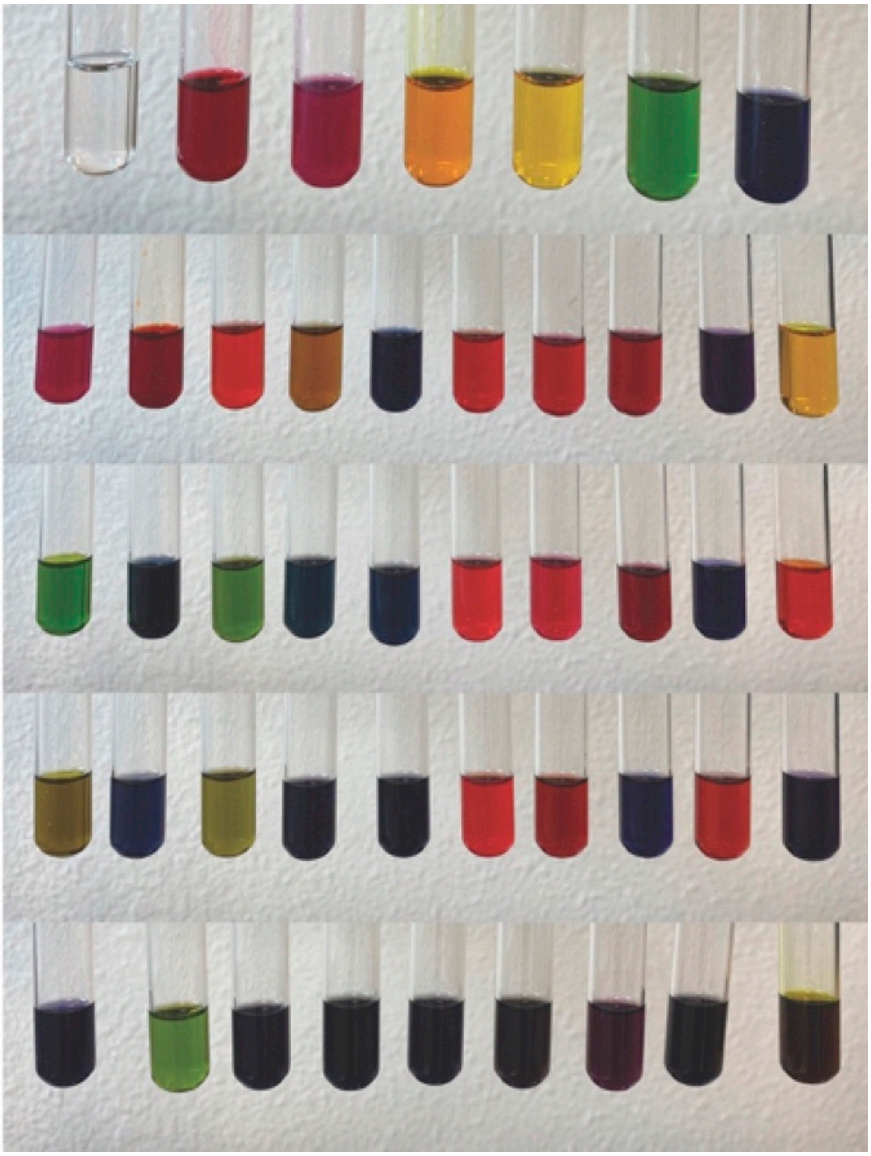


Figure S2. The 42 dye combinations from Section 2.1 plus the three optimized combinations from Section 3.2. Row 1 corresponds to a MeOH blank and combinations A:P, Row 2 corresponds to combinations AB:KM, Row 3 corresponds to combinations KC:AKM, Row 4 corresponds to combinations AKC:BMP and Row 5 corresponds to combinations BCP: ABKMCP. The remaining five combinations seen in Row 5 correspond to the three optimized dye combinations which are discussed in further detail in Sections 2.2 and 3.2.

Dye Sensitized Solar Cell Fabrication

DSSC's in this work were produced on FTO glass with TiO_2 anodes screen printed (83-100 mesh) using Solaronix Ti-Nanoxide pastes [1] (reference Figure 3). A blocking layer was first printed and fired with BL/SP (SKU: 17121) paste followed by a micro/nanocrystalline D/SP mix (SKU: 14121). The sintering process was performed on a hot plate in a fume hood by slowly heating the anodes to 450ºC (~5ºC/min) and firing for 15 minutes before being allowed to furnace cool back to room temperature [1]. Counter electrodes were also printed on FTO glass using Solaronix Plastisol (SKU: 41221) and heat treated in the same manner. The electrolyte was Solaronix Iodolyte AN-50 I^-/I_3^- (SKU: 31112). A photo of a final assembled DSSC is shown in Figure 4. For additional information about DSSC fabrication and general procedures in this work, reference [4].

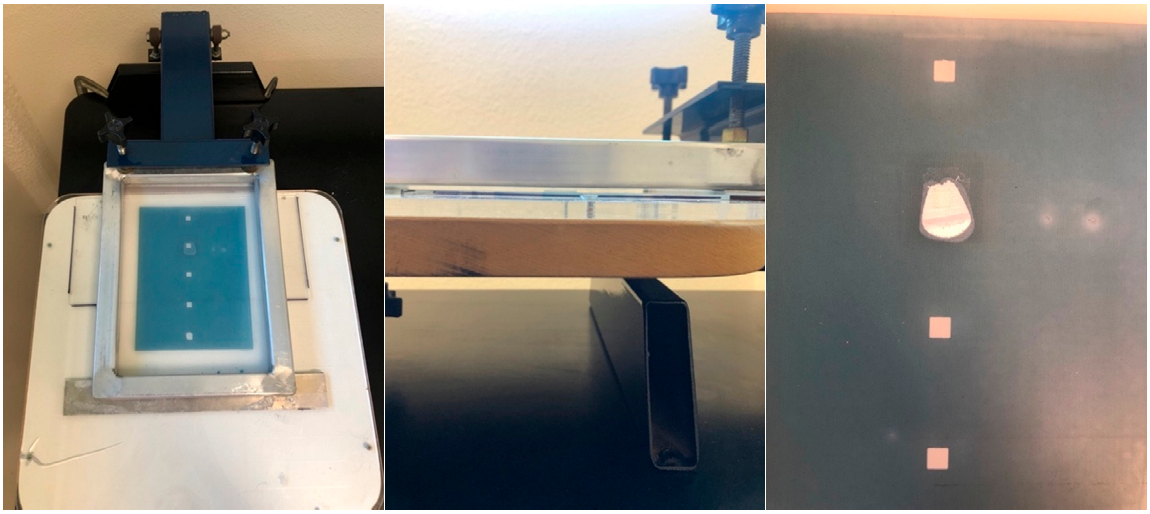


Figure S3. The screen printing apparatus used to produce the TiO_2 anodes and Pt counter electrodes showing the 83-100 mesh screen and blue photoemulsion mask (left). The snap-off distance of the screen was set to 2.5mm in accordance with the methods presented in [1] (center). Solaronix Ti-Nanoxide paste was applied over the mask and forced through the mesh onto the FTO glass using a hard rubber squeegee (right).

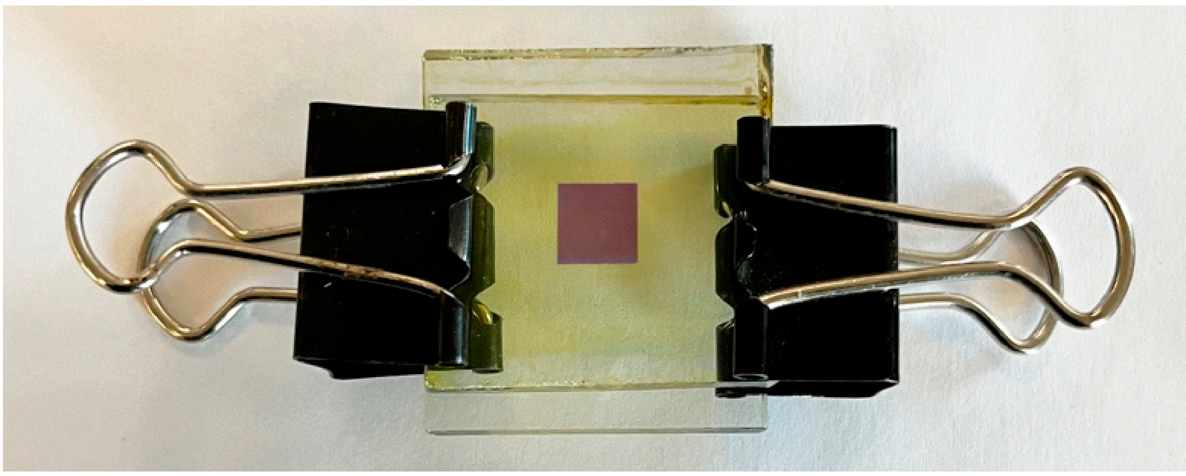
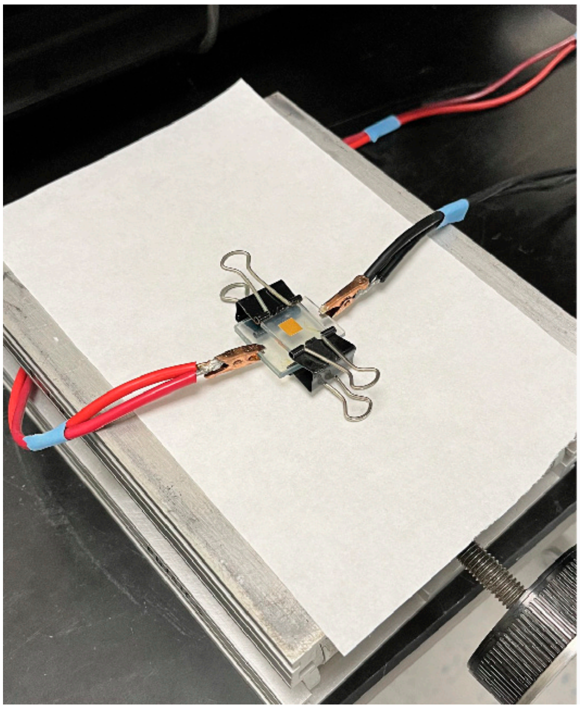


Figure S4. Photo of a final assembled DSSC sensitized with BK dye. The active anode area is 0.36 cm².

Making IV Measurements

IV measurements were made using a ScienceTech solar simulator with an AM1.5G filter and Keithley 2400 source meter unit (SMU). The power of the solar simulator was set to 1-Sun using an Abet Technologies Model 15151 reference PV cell which was calibrated to produce 100 mV at an irradiance of 100 mW/cm². DSSC's were then connected to the SMU via a 4-wire connection as shown in Figure 5.



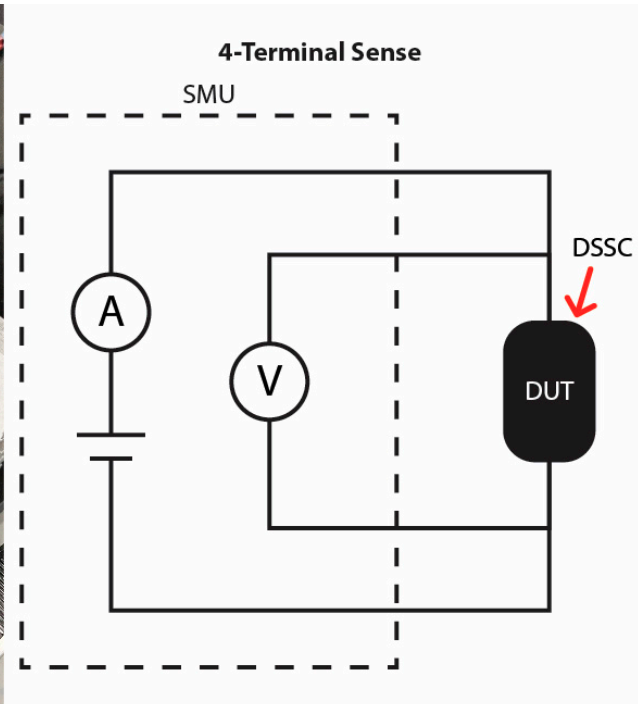
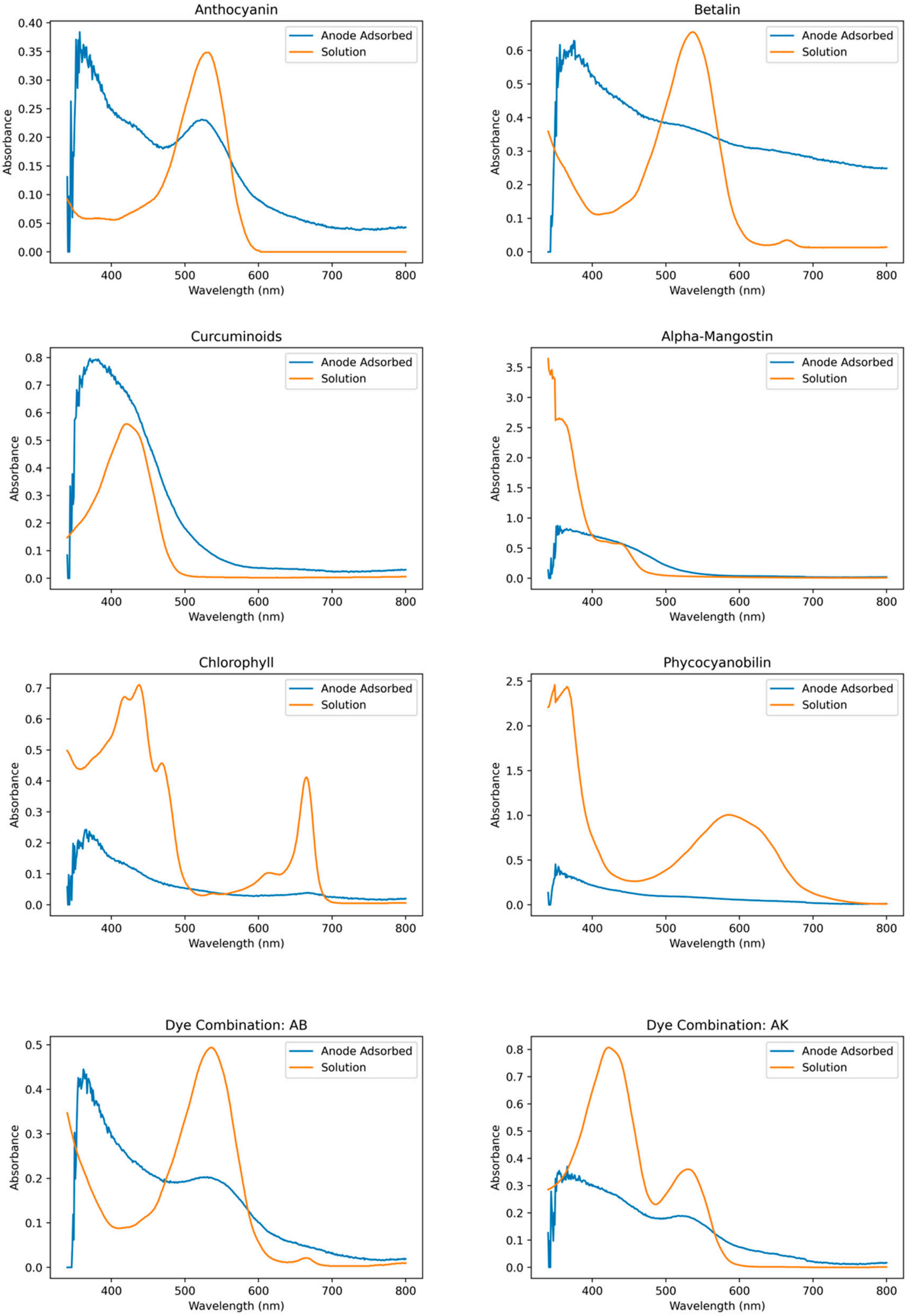
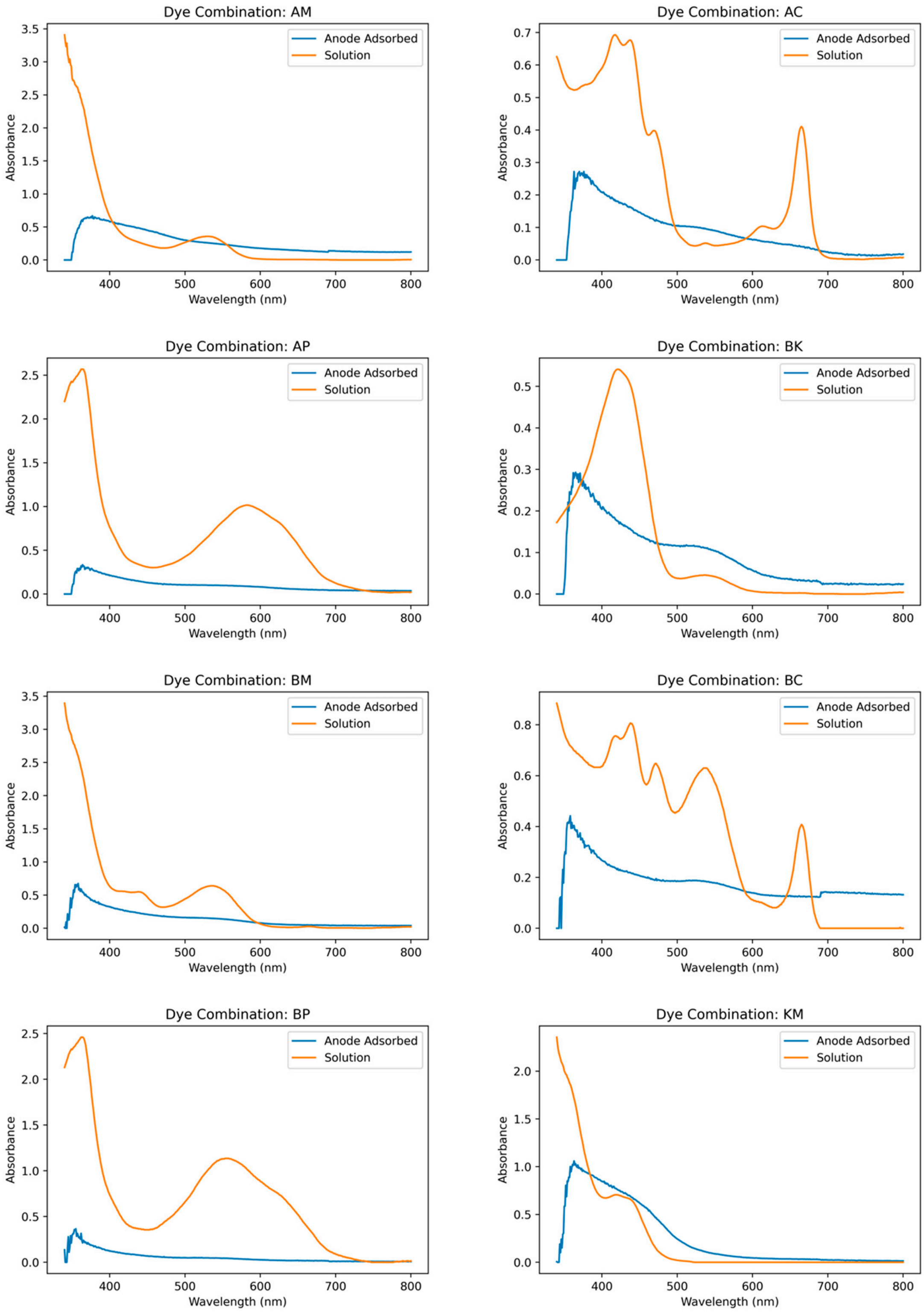


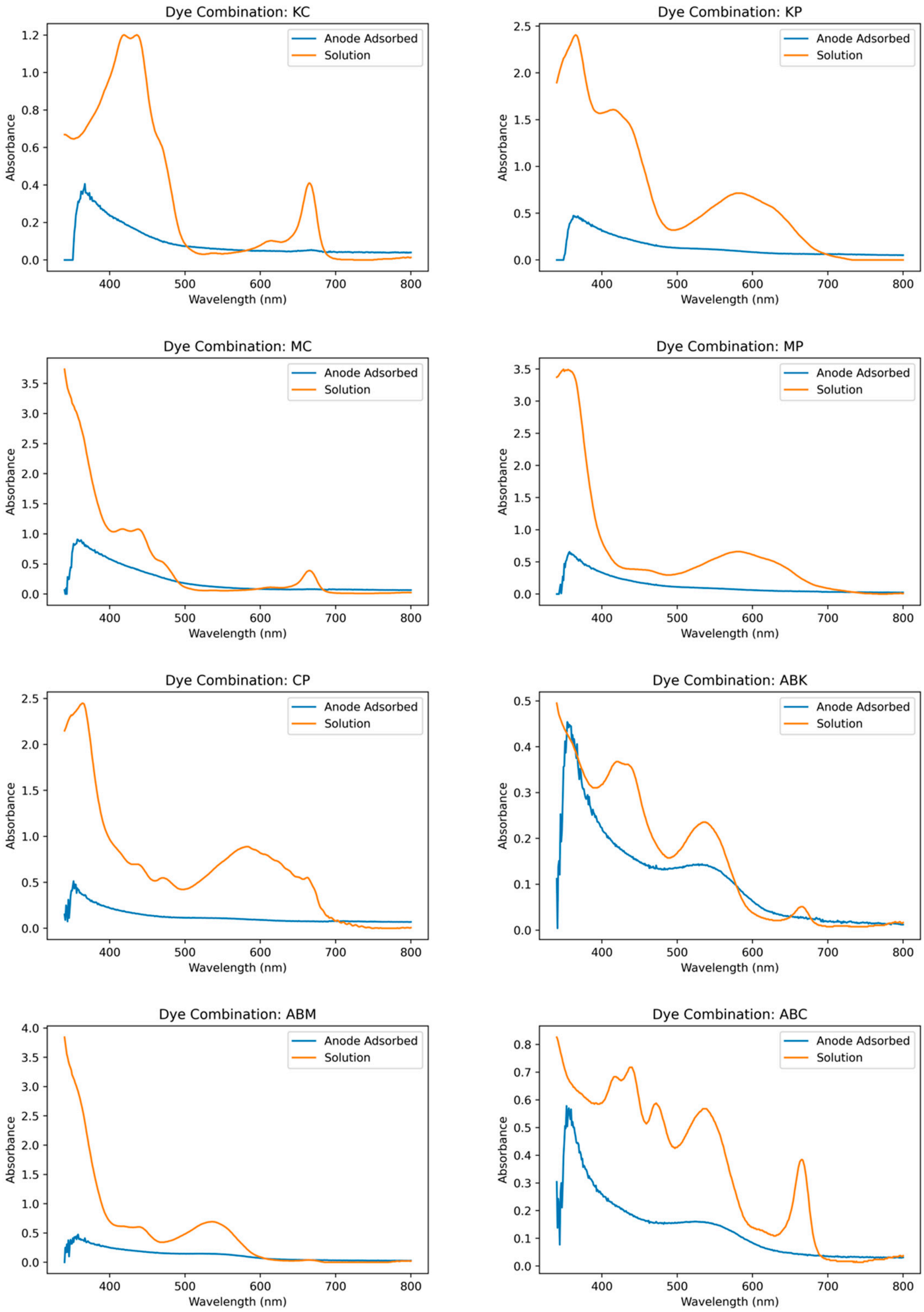
Figure S5. 4-wire connection of a DSSC (sensitized with KM) to the source meter unit (SMU) (left) and a schematic diagram of the 4-wire connection (right). This connection eliminates inherent lead and contact resistance and was found to yield a much less noisy and much more repeatable measurement than a simple 2-wire connection.

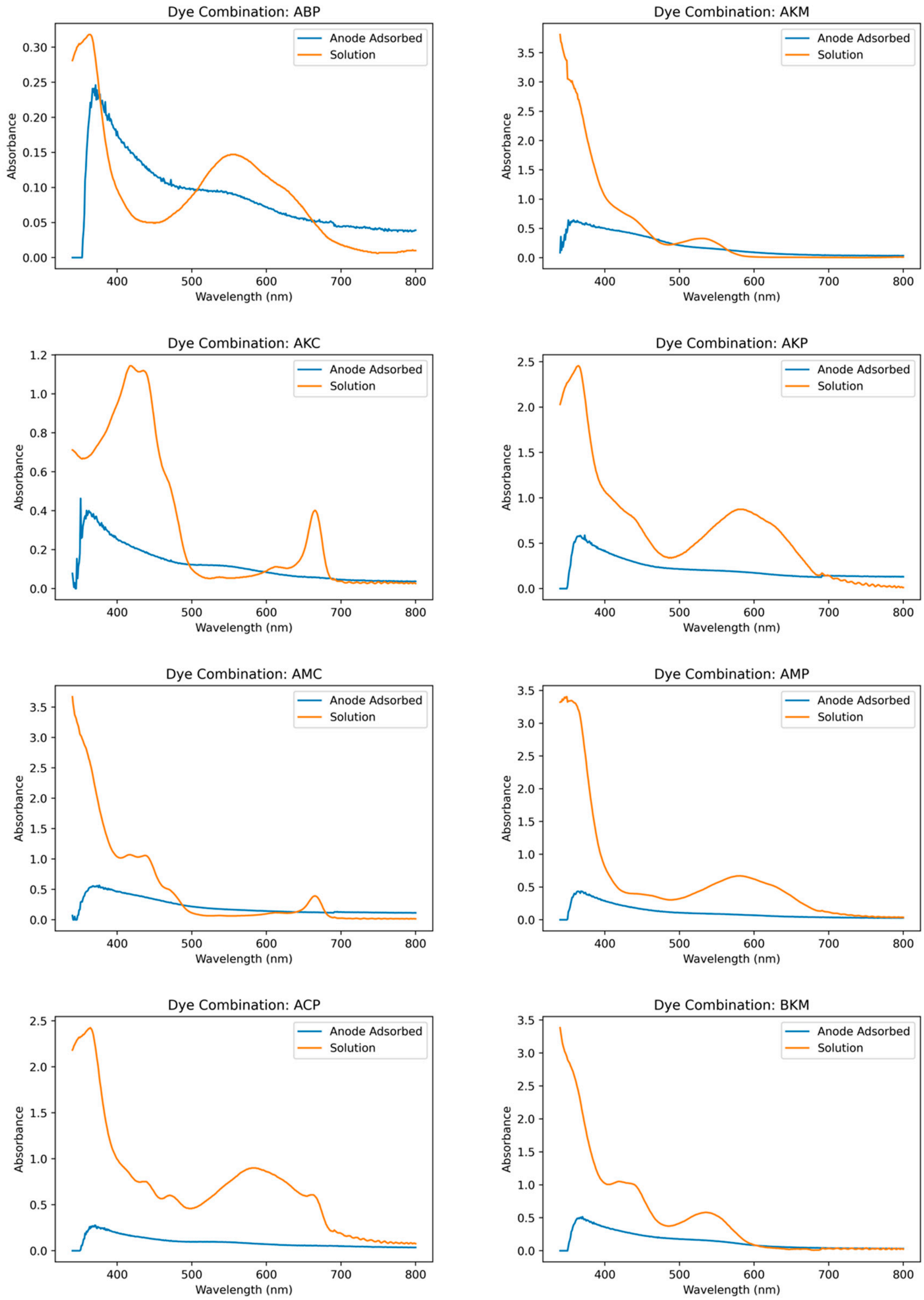
UV-Vis Data

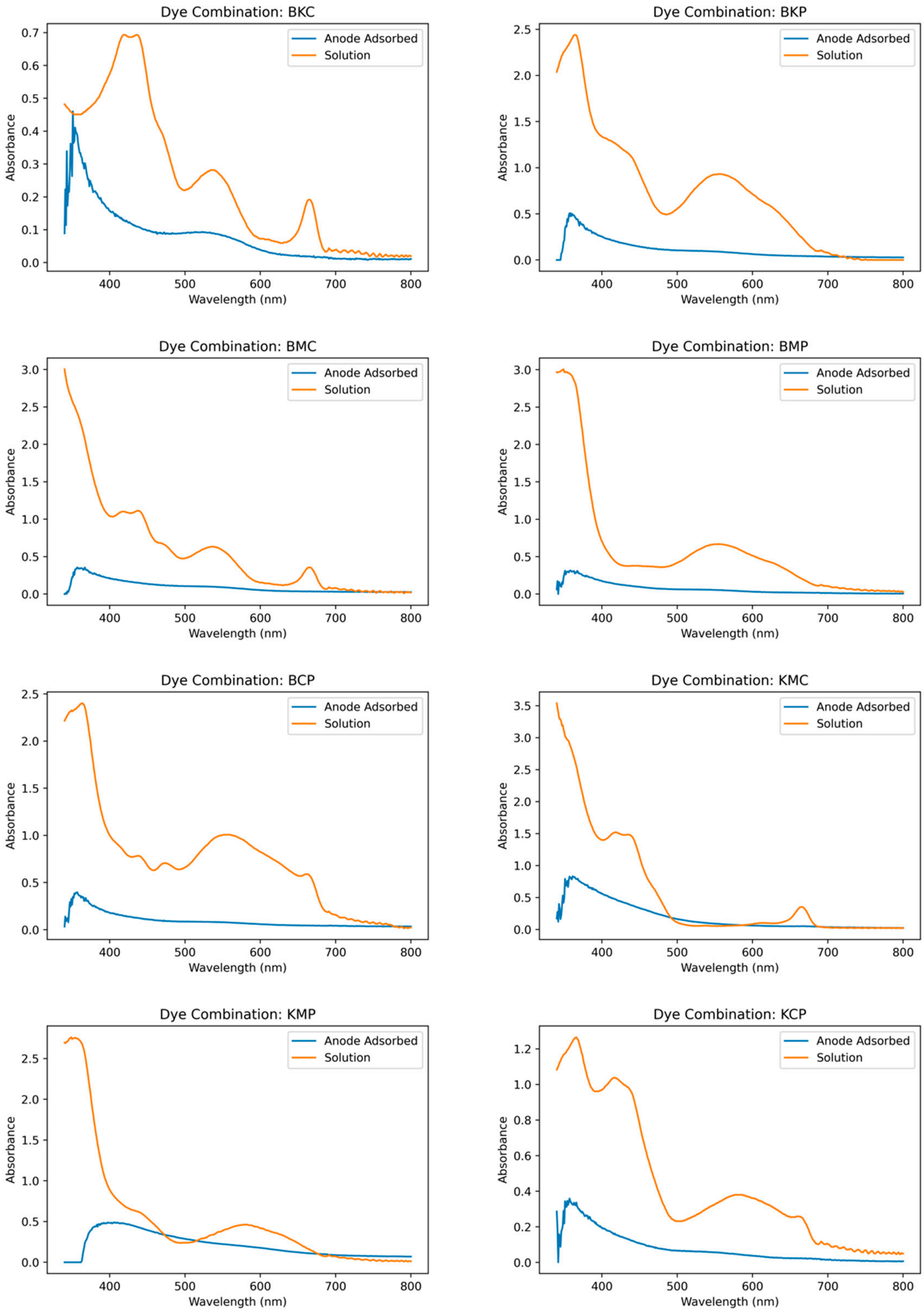
All UV-Vis data was collected with a Beckman Coulter DU730 spectrophotometer and a matched set of Quartz cuvettes for wavelengths between 340 and 800 nm. The anode adsorbed data was collected by sensitizing optically transparent TiO_2 anodes (made from Solaronix T/SP paste) and then masking the edges of the glass around the anode with painters tape to prevent light refraction around the anode which would result in T > 1. These measurement were of course blanked against an unsensitized anode. The UV-Vis results of each of the 42 dye combinations are shown below in Figure 6.


Anthocyanin
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Betalin
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Curcuminoids
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Alpha-Mangostin
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Chlorophyll
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Phycocyanobilin
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: AB
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: AK
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)


Dye Combination: AM
Dye Combination: AC
Dye Combination: AP
Dye Combination: BK
Dye Combination: BM
Dye Combination: BC
Dye Combination: BP
Dye Combination: KM
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
400
500
600
700
800


Dye Combination: KC
Dye Combination: KP
Dye Combination: MC
Dye Combination: MP
Dye Combination: CP
Dye Combination: ABK
Dye Combination: ABM
Dye Combination: ABC
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)


Dye Combination: ABP
Dye Combination: AKM
Dye Combination: AKC
Dye Combination: AKP
Dye Combination: AMC
Dye Combination: AMP
Dye Combination: ACP
Dye Combination: BKM
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)


Dye Combination: BKC
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: BKP
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: BMC
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: BMP
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: BCP
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: KMC
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: KMP
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)
Dye Combination: KCP
Anode Adsorbed
Solution
Absorbance
Wavelength (nm)

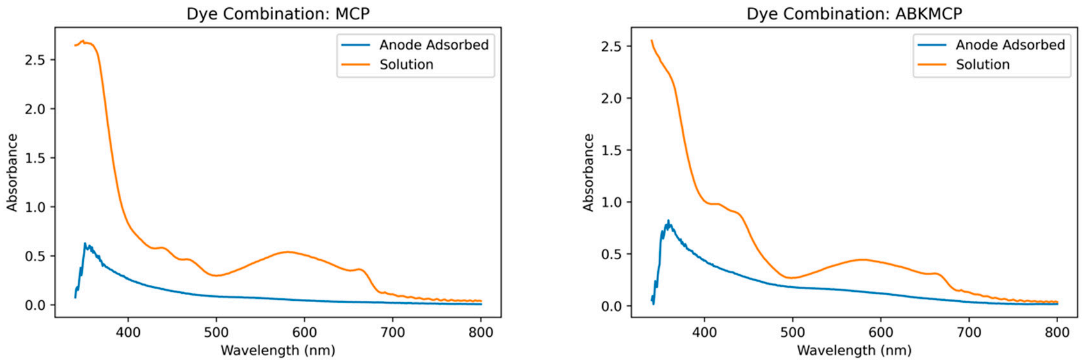
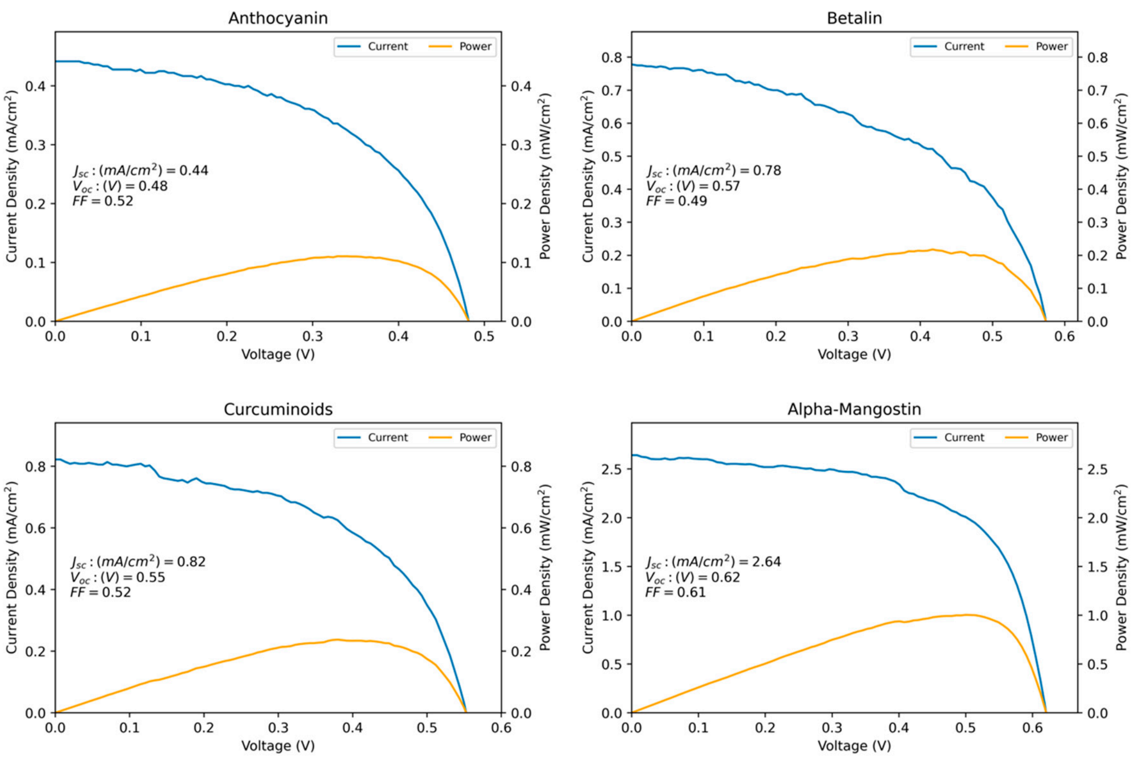
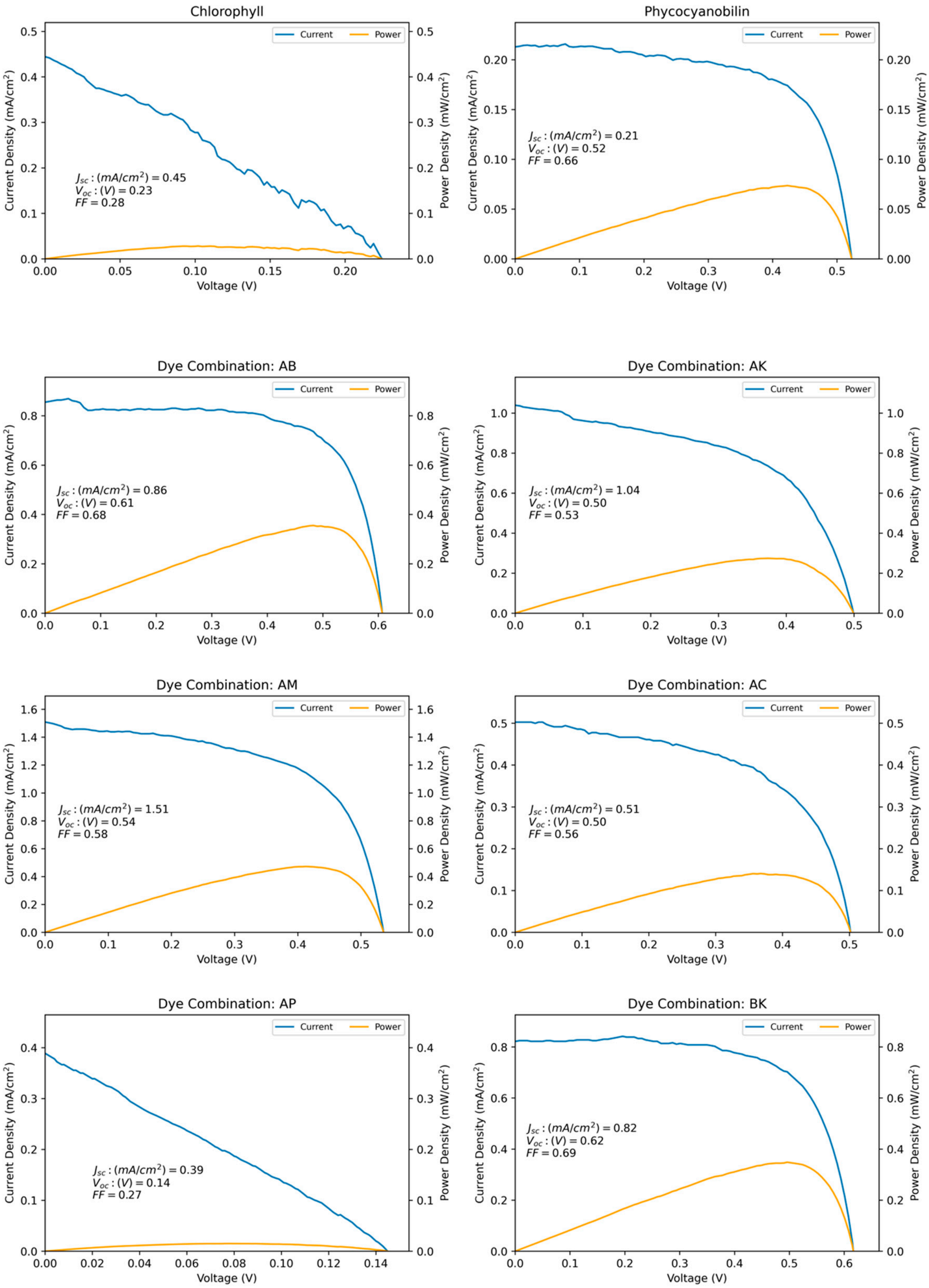


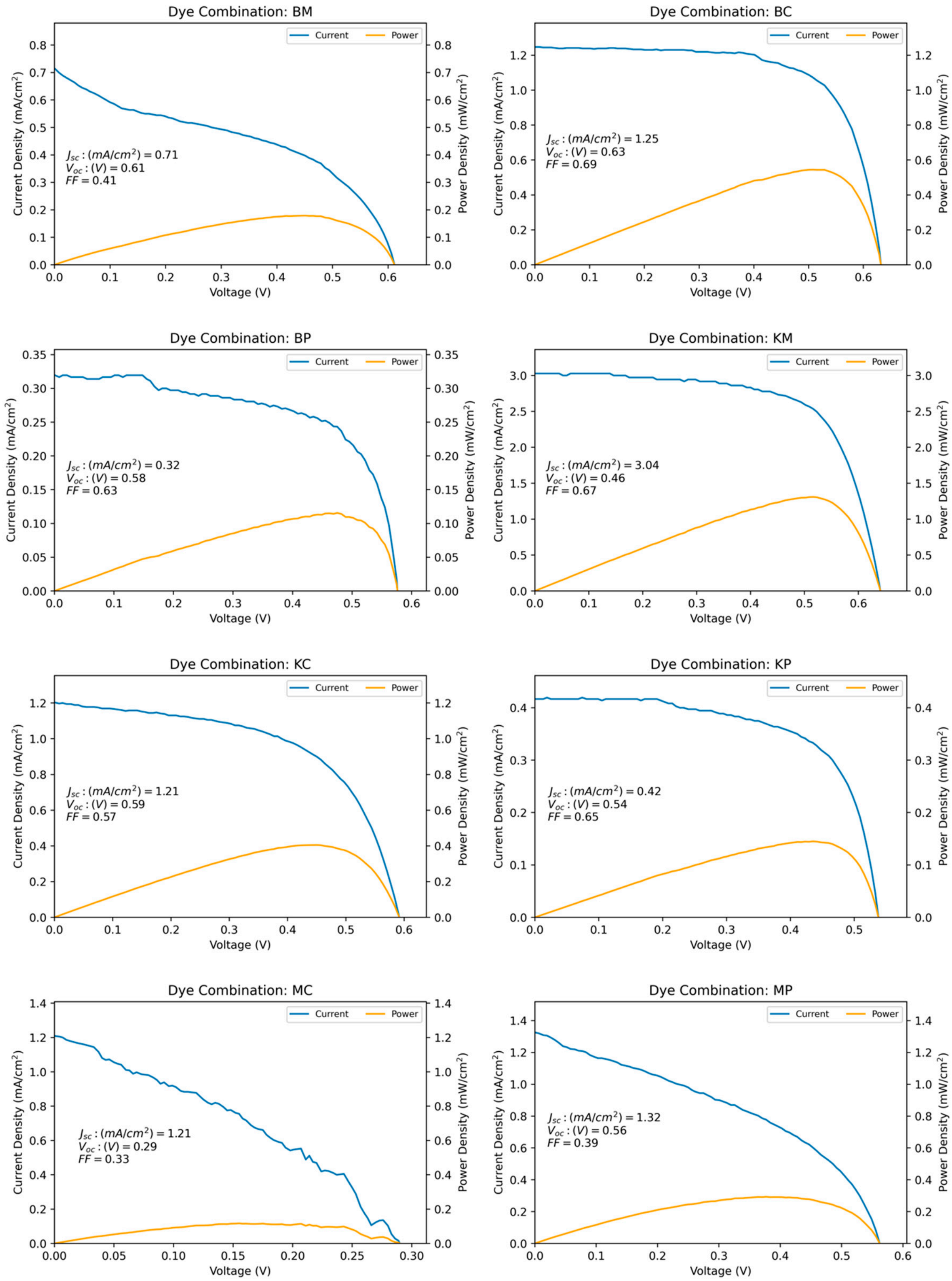
Figure S6. UV-Vis spectra of all 42 dye combinations from this work beginning with the individual dyes, then showing 1:1 combinations followed by 1:1:1 combinations, and finally showing the global ABKMCP combination. Spectra are shown for both the bulk solution and anode adsorbed regimes.

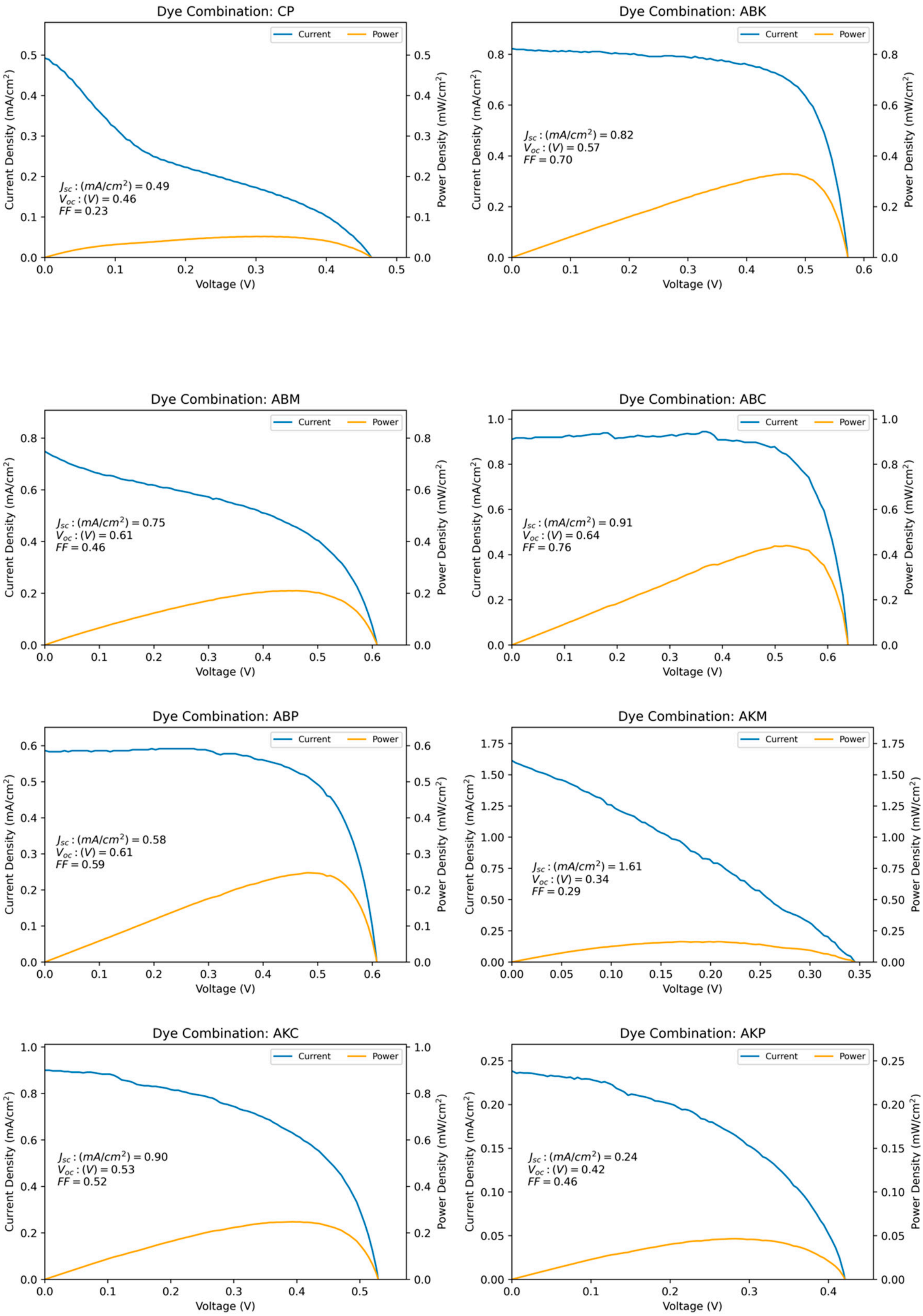
IV Measurements

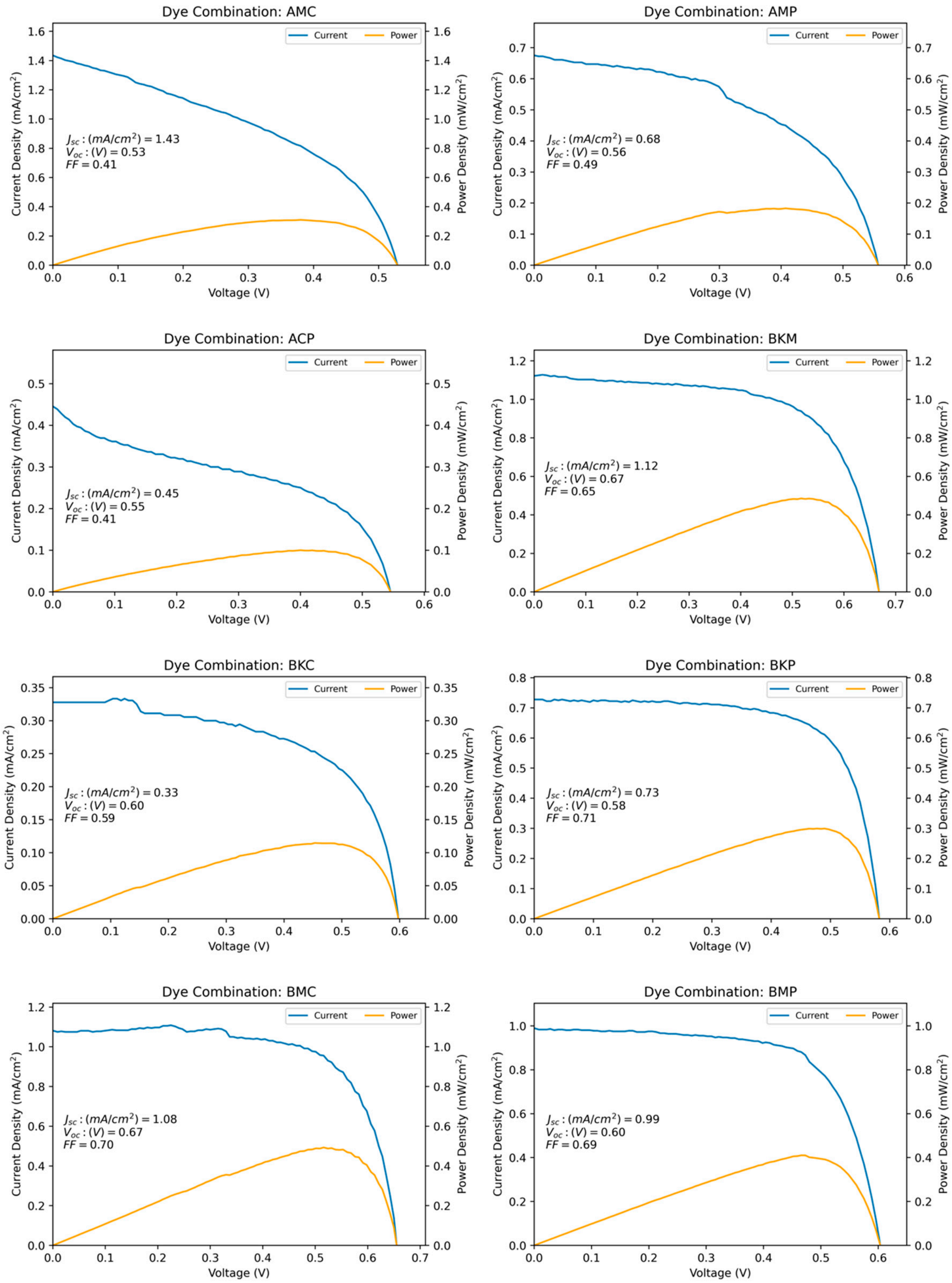
IV measurements were collected with an input power of 36 mW (0.36 cm² * 100 mW/cm²) using an AM1.5G filter. The IV results of each of the 42 dye combinations, as well as the optimized combinations, are shown below in Figure 7.

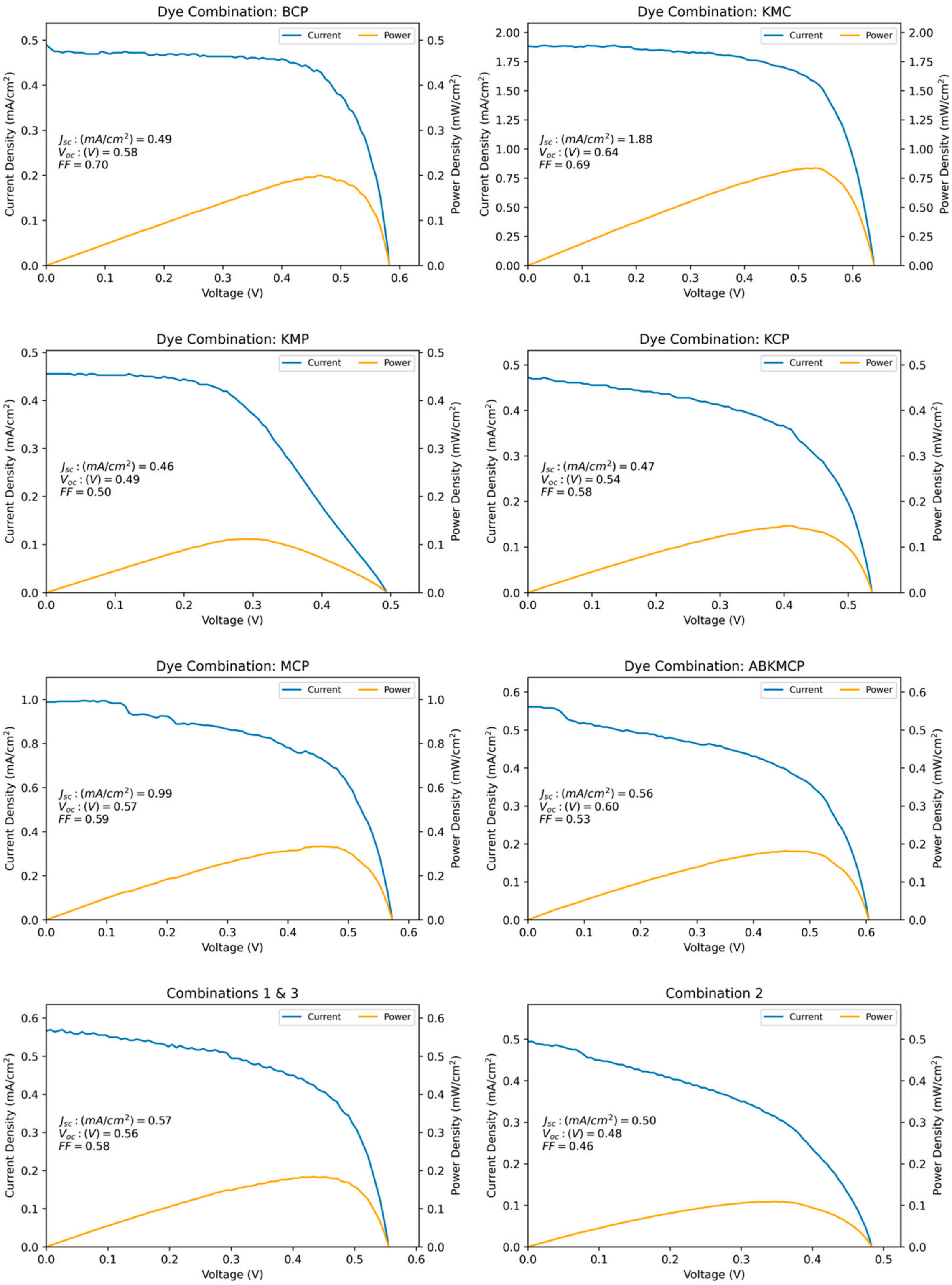



Chlorophyll
Current
Power
$J_{sc}: (mA/cm^2) = 0.45$
$V_{oc}: (V) = 0.23$
$FF = 0.28$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)
Phycocyanobilin
Current
Power
$J_{sc}: (mA/cm^2) = 0.21$
$V_{oc}: (V) = 0.52$
$FF = 0.66$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)
Dye Combination: AB
Current
Power
$J_{sc}: (mA/cm^2) = 0.86$
$V_{oc}: (V) = 0.61$
$FF = 0.68$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)
Dye Combination: AK
Current
Power
$J_{sc}: (mA/cm^2) = 1.04$
$V_{oc}: (V) = 0.50$
$FF = 0.53$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)
Dye Combination: AM
Current
Power
$J_{sc}: (mA/cm^2) = 1.51$
$V_{oc}: (V) = 0.54$
$FF = 0.58$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)
Dye Combination: AC
Current
Power
$J_{sc}: (mA/cm^2) = 0.51$
$V_{oc}: (V) = 0.50$
$FF = 0.56$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)
Dye Combination: AP
Current
Power
$J_{sc}: (mA/cm^2) = 0.39$
$V_{oc}: (V) = 0.14$
$FF = 0.27$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)
Dye Combination: BK
Current
Power
$J_{sc}: (mA/cm^2) = 0.82$
$V_{oc}: (V) = 0.62$
$FF = 0.69$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)


Dye Combination: BM
Current
Power
$J_{sc}:(mA/cm^2) = 0.71$
$V_{oc}:(V) = 0.61$
$FF = 0.41$
Dye Combination: BC
$J_{sc}:(mA/cm^2) = 1.25$
$V_{oc}:(V) = 0.63$
$FF = 0.69$
Dye Combination: BP
$J_{sc}:(mA/cm^2) = 0.32$
$V_{oc}:(V) = 0.58$
$FF = 0.63$
Dye Combination: KM
$J_{sc}:(mA/cm^2) = 3.04$
$V_{oc}:(V) = 0.46$
$FF = 0.67$
Dye Combination: KC
$J_{sc}:(mA/cm^2) = 1.21$
$V_{oc}:(V) = 0.59$
$FF = 0.57$
Dye Combination: KP
$J_{sc}:(mA/cm^2) = 0.42$
$V_{oc}:(V) = 0.54$
$FF = 0.65$
Dye Combination: MC
$J_{sc}:(mA/cm^2) = 1.21$
$V_{oc}:(V) = 0.29$
$FF = 0.33$
Dye Combination: MP
$J_{sc}:(mA/cm^2) = 1.32$
$V_{oc}:(V) = 0.56$
$FF = 0.39$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)


Dye Combination: CP
Current
Power
$J_{sc}:(mA/cm^2) = 0.49$
$V_{oc}:(V) = 0.46$
$FF = 0.23$
Dye Combination: ABK
$J_{sc}:(mA/cm^2) = 0.82$
$V_{oc}:(V) = 0.57$
$FF = 0.70$
Dye Combination: ABM
$J_{sc}:(mA/cm^2) = 0.75$
$V_{oc}:(V) = 0.61$
$FF = 0.46$
Dye Combination: ABC
$J_{sc}:(mA/cm^2) = 0.91$
$V_{oc}:(V) = 0.64$
$FF = 0.76$
Dye Combination: ABP
$J_{sc}:(mA/cm^2) = 0.58$
$V_{oc}:(V) = 0.61$
$FF = 0.59$
Dye Combination: AKM
$J_{sc}:(mA/cm^2) = 1.61$
$V_{oc}:(V) = 0.34$
$FF = 0.29$
Dye Combination: AKC
$J_{sc}:(mA/cm^2) = 0.90$
$V_{oc}:(V) = 0.53$
$FF = 0.52$
Dye Combination: AKP
$J_{sc}:(mA/cm^2) = 0.24$
$V_{oc}:(V) = 0.42$
$FF = 0.46$
Current Density (mA/cm^2)
Power Density (mW/cm^2)
Voltage (V)


Dye Combination: AMC
Current
Power
Jsc : (mA/cm2) = 1.43
Voc : (V) = 0.53
FF = 0.41
Current Density (mA/cm2)
Power Density (mW/cm2)
Voltage (V)
Dye Combination: AMP
Jsc : (mA/cm2) = 0.68
Voc : (V) = 0.56
FF = 0.49
Dye Combination: ACP
Jsc : (mA/cm2) = 0.45
Voc : (V) = 0.55
FF = 0.41
Dye Combination: BKM
Jsc : (mA/cm2) = 1.12
Voc : (V) = 0.67
FF = 0.65
Dye Combination: BKC
Jsc : (mA/cm2) = 0.33
Voc : (V) = 0.60
FF = 0.59
Dye Combination: BKP
Jsc : (mA/cm2) = 0.73
Voc : (V) = 0.58
FF = 0.71
Dye Combination: BMC
Jsc : (mA/cm2) = 1.08
Voc : (V) = 0.67
FF = 0.70
Dye Combination: BMP
Jsc : (mA/cm2) = 0.99
Voc : (V) = 0.60
FF = 0.69


Dye Combination: BCP
Current
Power
$J_{sc}: (mA/cm^2) = 0.49$
$V_{oc}: (V) = 0.58$
$FF = 0.70$
Dye Combination: KMC
$J_{sc}: (mA/cm^2) = 1.88$
$V_{oc}: (V) = 0.64$
$FF = 0.69$
Dye Combination: KMP
$J_{sc}: (mA/cm^2) = 0.46$
$V_{oc}: (V) = 0.49$
$FF = 0.50$
Dye Combination: KCP
$J_{sc}: (mA/cm^2) = 0.47$
$V_{oc}: (V) = 0.54$
$FF = 0.58$
Dye Combination: MCP
$J_{sc}: (mA/cm^2) = 0.99$
$V_{oc}: (V) = 0.57$
$FF = 0.59$
Dye Combination: ABKMCP
$J_{sc}: (mA/cm^2) = 0.56$
$V_{oc}: (V) = 0.60$
$FF = 0.53$
Combinations 1 & 3
$J_{sc}: (mA/cm^2) = 0.57$
$V_{oc}: (V) = 0.56$
$FF = 0.58$
Combination 2
$J_{sc}: (mA/cm^2) = 0.50$
$V_{oc}: (V) = 0.48$
$FF = 0.46$
Current Density (mA/cm²)
Power Density (mW/cm²)
Voltage (V)

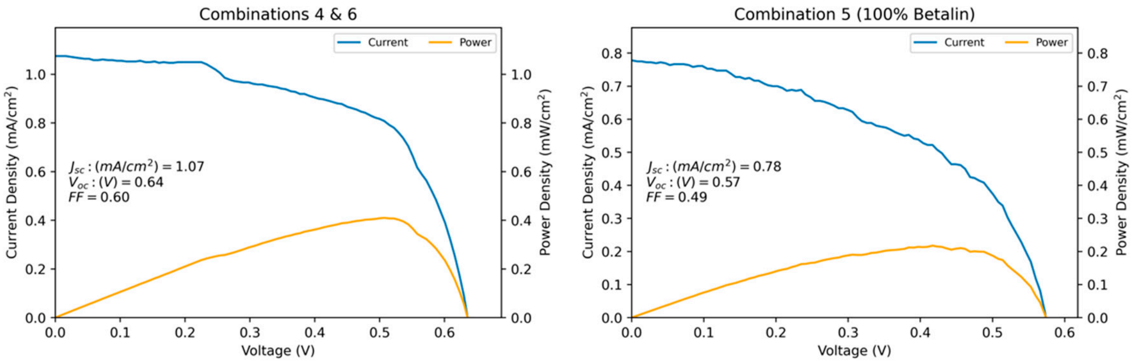


Figure 7. IV data for all 42 dye combinations from this work beginning with the individual dyes, then showing 1:1 combinations followed by 1:1:1 combinations, and finally showing the global ABKMCP combination. The IV data for the six optimized combinations are also shown. The open circuit voltage, short circuit current and fill factor are indicated on each plot, as well as Table 6.

References

1. Obi, K.; Frolova, L.; Fuierer, P. Preparation and performance of prickly pear (Opuntia phaeacantha) and mulberry (Morus rubra) dye-sensitized solar cells. *Sol. Energy* **2020**, *208*, 312–320. https://doi.org/10.1016/j.solener.2020.08.006.
2. Zaffino, C., Russo, B., Bruni, S. Surface-enhanced Raman scattering (SERS) study of Anthocyanidins. *Molecular and Biomolecular Spectroscopy* **2015**, 149, 41-47. https://doi.org/1016/j.saa.2015.04.039.
3. Nakano, S., Sugimoto, N. The structural stability and catalytic activity of DNA and RNA oligonucleotides in the presence of organic solvents. *Biophysical Reviews* **2016**, 8, 11-23. https://doi.org/10.1007/s12551-015-0188-0.
4. Manz, N. Optimizing the Combination of Natural Pigments for Co-Sensitization of Panchromatic TiO2 Dye Sensitized Solar Cells. M.S. Thesis, New Mexico Institute of Mining and Technology, Socorro, NM, USA, April 2022.