Electronic Supplementary Information

The Photobioelectrochemical Activity of Thylakoid Bioanodes is Increased *via* Photocurrent Generation and Improved Contacts by Membrane-Intercalating Conjugated Oligoelectrolytes

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COE	COE1-3C	COE1-4C	COE1-5C	COE2-3C	COE2-4C	COE2-5C	COE3-4C
λ_{max} (nm)	407	418	425	357	374	385	400
ε (M^{-1} cm^{-1})	85395	69430	76020	62582	29136	65060	37727
λ_{onset} (nm)	467	500	511	395	442	466	503
E_{gap} (eV)	2.66	2.48	2.43	3.14	2.81	2.66	2.47

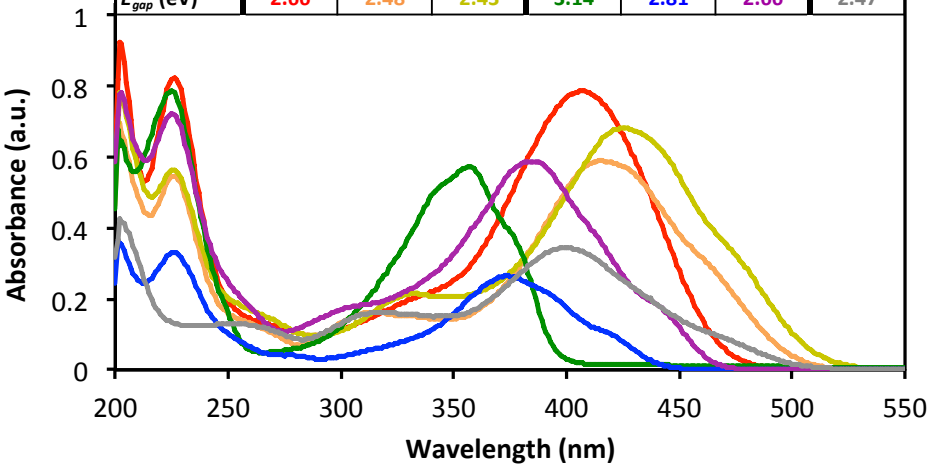

Fig. S1. Aqueous UV-vis absorbance spectra and optoelectronic properties of all seven COE molecules. Note the red-shifted spectra of COE-1 type molecules relative to COE-2 type.[1,2] [COE] = 9 μM in 100 mM, pH = 7.4 phosphate buffer. (Table, inset) A summary of the absorbance maxima (λ_{max}), extinction coefficient at λ_{max} (ε), absorbance onset (λ_{onset}), and optical gap (E_{gap}) for each of the COEs is displayed. Note that these spectra are not normalized, so ε is correlated to the peak height at λ_{max}.

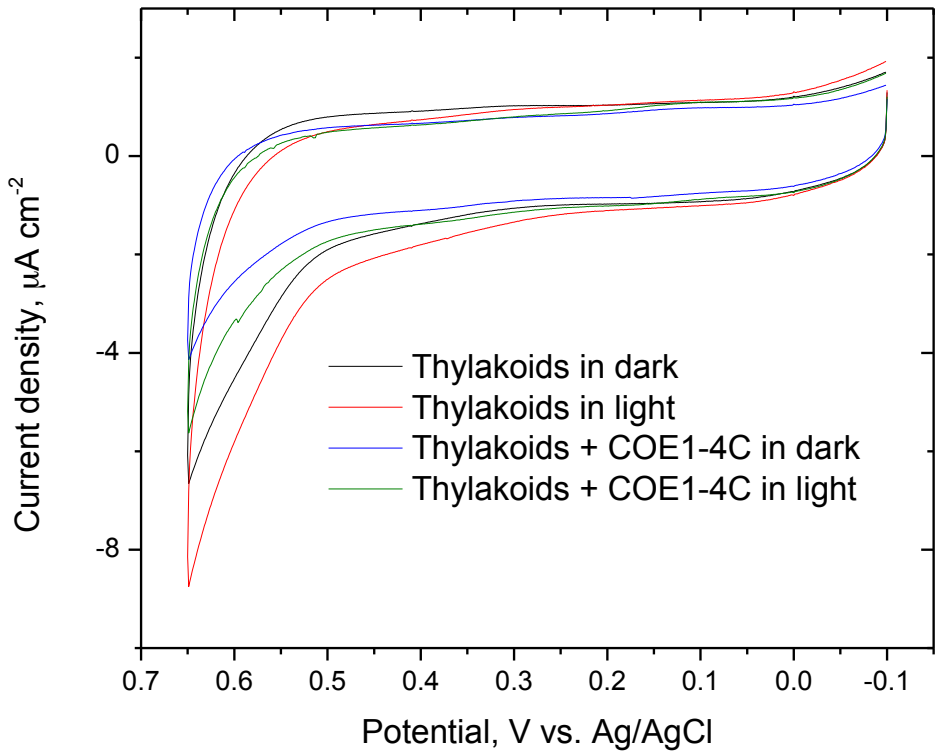

Fig. S2. Representative dark and light CV of thylakoid and thylakoid/COE electrodes. Buffer was 100 mM, pH 7.4 phosphate; scan rate = 10 mV/s.

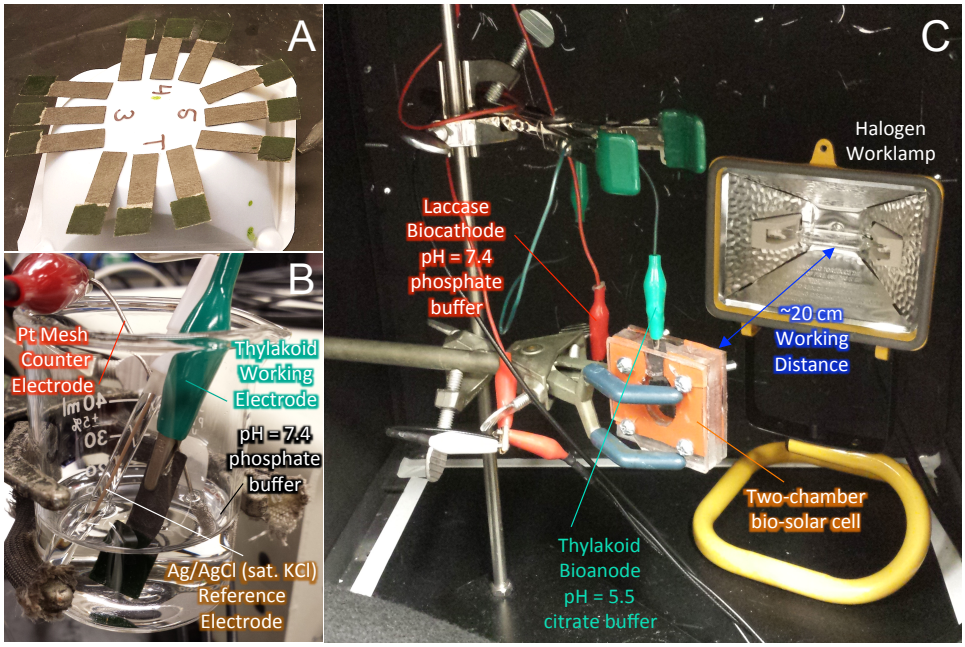

Fig. S3. Experimental Systems. (A) Drying working electrodes, constructed from 50 μL aliquots of thylakoids (unmodified and modified with COE1-3C, -4C, and -5C) drop cast on 1 cm × 1 cm Toray® carbon paper. This image was taken immediately prior to incubation with tetramethyl orthosilicate (silica layer deposition). (B) The three-electrode setup for electrochemical testing of the thyalkoid and thylakoid/COE working electrodes. (C) The chamber used for light- and dark-current measurements of thylakoid and thylakoid/COE working electrodes during amperometry and bio-solar cell testing. A two-chamber solar cell device[3] is pictured. The lamp is a 250 W halogen rated to 5200 lumens.

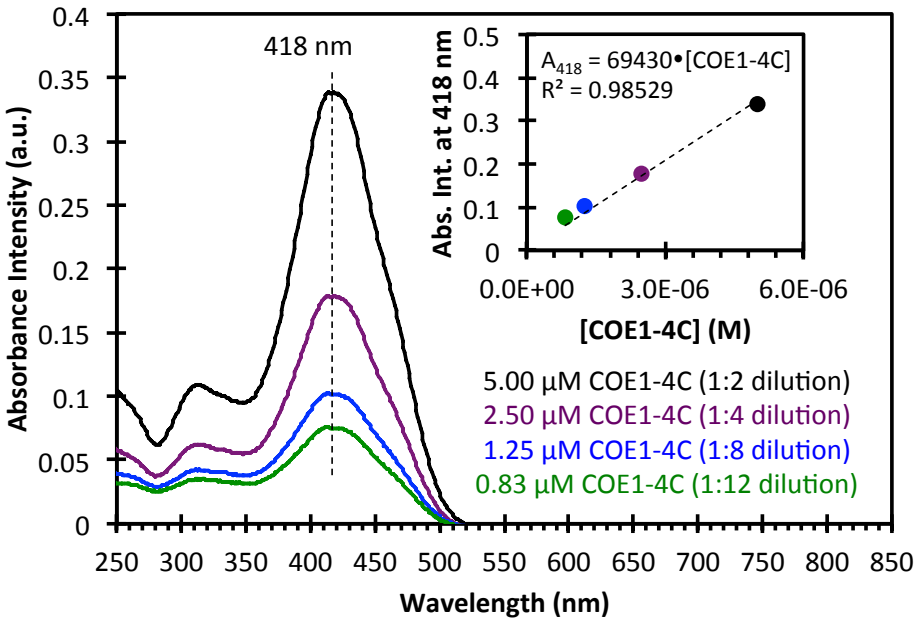

Fig. S4. Aqueous COE1-4C absorption concentration dependence. Solvent was 100 mM, pH = 7.4 phosphate buffer. The calibration curve (inset) at the absorbance maximum of 418 nm indicates an extinction coefficient of 69430 L mol^{-1} cm^{-1}.

References

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2 P. Beaujuge, C. Amb and J. R. Reynolds, *Acc. Chem. Res.*, 2010, **43**, 1396–1407.
3 M. Rasmussen, A. Shrier and S. D. Minteer, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9062–5.