Supporting Information for:

Photo-Assisted Electrodeposition of MoS₂ from Ionic Liquid on Organic-Functionalized Silicon Photoelectrodes for H₂ Generation

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Figure S1. Water contact angle of (a) *p*-Si(111)|diOMe and (b) *p*-Si(111)|Ph surfaces with a 10 μ L water drop.



Figure S2. X-ray photoelectron spectrum of (a) Si 2*p* and (b) C 1*s* for *p*-Si(111)|diOMe surface, and depiction of organic molecules attached to Si(111) for (c) *p*-Si(111)|Ph and (d) *p*-Si(111)|diOMe.



Figure S3. (a) Nyquist plots for *p*-Si(111)|Ph (black) and *p*-Si(111)|diOMe (red) surfaces. (b) Representation of the different resistances determined by EIS and plotted versus the applied potential. Conditions: Ag-wire reference electrode, 5 mM ethyl viologen in 0.1 M LiClO₄/MeCN, 1-sun irradiation, 10 mV AC amplitude, $10^5 < f < 0.1$ Hz. (c) Nyquist Plot for *p*-Si(111)|CH₃ at *E* = -0.3 V vs. SCE. (d) Potential dependence of charge transfer resistance of *p*-Si(111)|CH₃ as determined by EIS. Conditions: 0.5 M H₂SO₄, 1-sun irradiation, 10 mV AC amplitude, frequency range $10^5 < f < 0.1$ Hz.



Figure S4. First scan of cyclic voltammogram and derivative cyclic voltabsorptometry of 0.005 M [MePipH]₂[MoS₄] in the (a) absence and (b) presence of 0.2 M [PipH][TFSI], $\lambda = 600$ nm, scan rate = 50 mV/s.



Figure S5. Effect of LED light on the open circuit potential of (a) *p*-Si|diOMe and (b) *p*-Si(111)|Ph with 0.005 M [MePipH]₂[MoS₄] and 0.2 M [PipH][TFSI] in EMIM-TFSI. (c) Cyclic voltammogram depicting anodic stability of bare *p*-Si(111) in 0.002 M ferrocene in EMIM-TFSI. (d) CV deposition of MoS_x on *p*-Si(111)|Ph and (e) first scan of the CV deposition on *p*-Si(111)|Ph with alternating light on and off with 0.005 M [MePipH]₂[MoS₄] and 0.2 M [PipH][TFSI] in EMIM-TFSI, scans 1-5, 10, 20, 30, 40, 50. Scan rate = 50 mV/s.



Figure S6. XPS survey spectra of (a) p-Si(111)|diOMe|MoS_x and (b) p-Si(111)|Ph|MoS_x. High resolution XPS spectrum of (c) Mo 3*d* and (d) S 2*p* regions of p-Si(111)|Ph|MoS_x.



Figure S7. Raman spectra of (a) p-Si(111)|diOMe|MoS_x, (b) p-Si(111)|Ph|MoS_x, and (c) GC|MoS_x.



Figure S8. Atomic force microscopy height retraces of (a) p-Si(111)|diOMe|MoS_x and (b) p-Si(111)|Ph|MoS_x.



Figure S9: PEC-HER test of p-Si(111)|H|MoS_x in 0.5 M H₂SO₄ (1-sun irradiation, scan rate = 100 mV/s), indicating instability of the hydride-terminated surface during catalytic conditions.