Supporting information for

Photoelectric Conversion based on Proton-Coupled Electron Transfer Reactions

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Experimental Section

Reagents. Indium tin oxide coated glasses (surface resistivity 8-12 Ω/sq), 1′,3′-Dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (Sp1), 1′,3′-Dihydro-8-methoxy-1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-(2H)-indole] (Sp2), hydroquinone (H_2Q), p-benzoquinone (Q), 2,3,5,6-tetrabromo-(1,4)benzoquinone (BrQ), tetrabromohydroquinone (BrH_2Q), tetrachlorohydroquinone (ClH_2Q), tetrachloro-1,4-benzoquinone (ClQ), tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$), N,N-dimethylformamide (DMF) and acetonitrile (MeCN) were purchased from Sigma-aldrich. Solutions were prepared by dissolving appropriate salts in deionized water.

Instrumentations and Measurements. UV light was obtained from a UV led (365 nm ± 10 nm) or from Lambda DG-4 Plus Xenon Source (Sutter Instruments) with a ZET365/20x filter from Chroma Inc.. Visible light was obtained from Lambda DG-4 Plus Xenon Source equipped with a FF02-409 blocking edge BrightLine® long-pass filter (Semrock Inc.). Rapid switching between UV light and visible light was achieved with Lambda DG-4. The absorbance was measured with a UV-Vis spectrometer (SPECORD 250 plus, Analytic Jena, AG, Germany).

The photoelectric conversion cell was homemade with two pieces of ITO glass separated by a silicon rubber joint (2 mm in thickness). A total surface area of 2 cm^2 was used for light illumination. The surface of the ITO coated glass was connected with copper wire through conductive epoxy glue.

An Autolab (Mettler-Toledo AG, Schwerzenbach, Switzerland) was used to measure the photocurrent. To evaluate the short circuit current, the working electrode and the ground electrode from the Autolab were connected to the two ITO electrodes. Open-circuit voltage was measured with an EMF-16 precision electrochemistry EMF interface from Lawson Labs Inc. To generate alternating currents, the incident light was switched from UV to visible repeatedly with fixed time intervals on one ITO electrode surface or with one ITO electrode illuminated with the UV led and the other with UV from DG-4 switching between on and off with fixed time intervals. Energy of light is measured with a power meter (FieldMaster, Coherent®, USA).

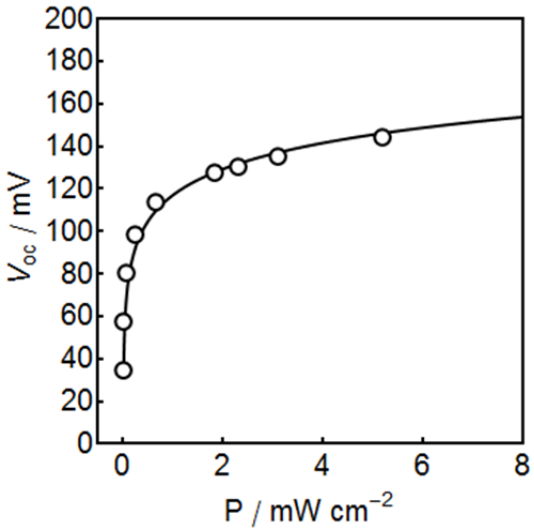

Figure S1. Open-circuit voltage dependence on UV light input power for a PCET based solar cell containing Sp1 (0.04 M), Q (0.01M), H_2Q (0.01 M) and $Bu_4N^+PF_6^-$ (0.1 M) in MeCN.

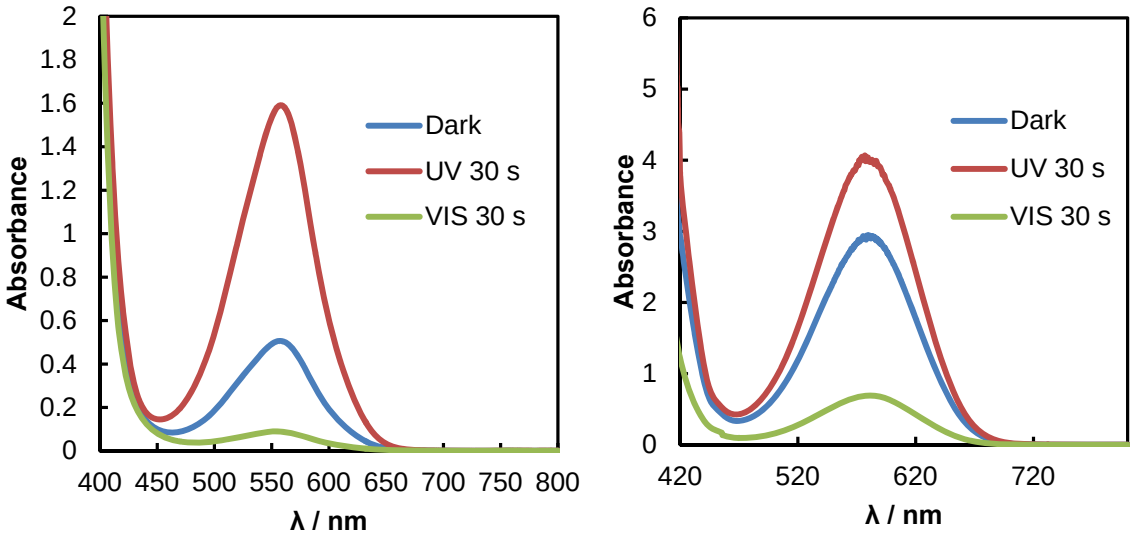

Figure S2. Absorption spectra in open circuit condition for cell composition in the dark, after 30 s UV illumination and after 30 s VIS illumination. (left): Sp1 0.04 M, Q 0.01 M, H_2Q 0.01 M and Bu_4NPF_6 0.1 M. (right): Sp2 0.03 M, BrQ 0.01 M, BrH_2Q 0.01 M. Solvent: MeCN.

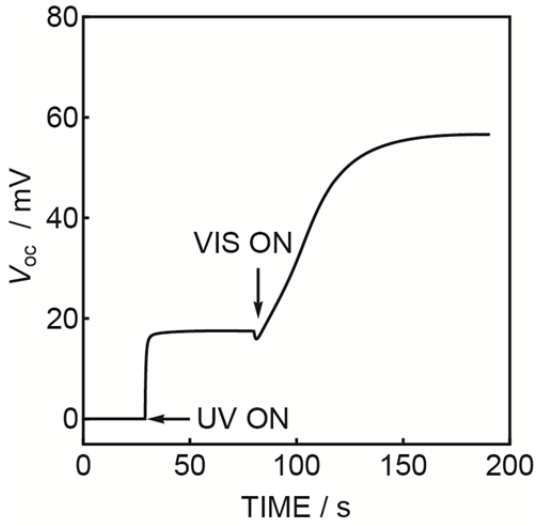

Figure S3. Open-circuit voltage evolution for a composition containing Sp2 (0.03 M), BrQ (0.01), BrH_2Q (0.01) and $Bu_4N^+PF_6^-$ (0.1M) in DMF with UV (365 nm±10 nm, 5 mW cm^{-2}) at one side and visible light (VIS, >409 nm, 10 mW cm^{-2}) at the other.

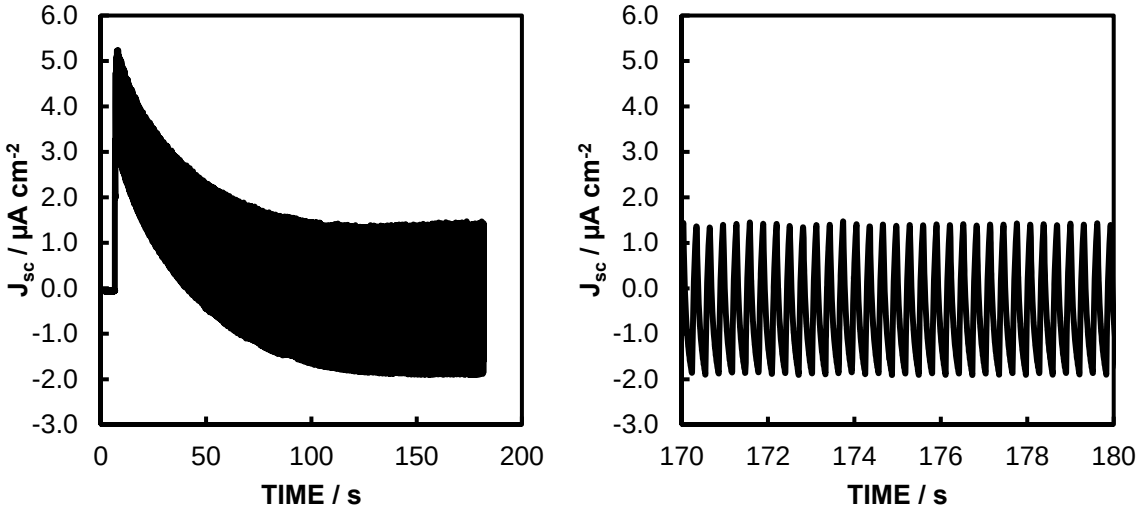

Figure S4. (left) Alternating current generation from PCET based solar cell containing 0.02 M BrQ/BrH_2Q, 0.08 M Sp2 and 0.1 M $Bu_4N^+PF_6^-$ in DMF. UV (5 mW cm^{-2} ,0.5 s) and VIS (10 mW cm^{-2}, 1 s) was alternatingly illuminating on one side of the ITO electrode. (right) Zooming from 170 s to 180 s from Fig. S3(left).

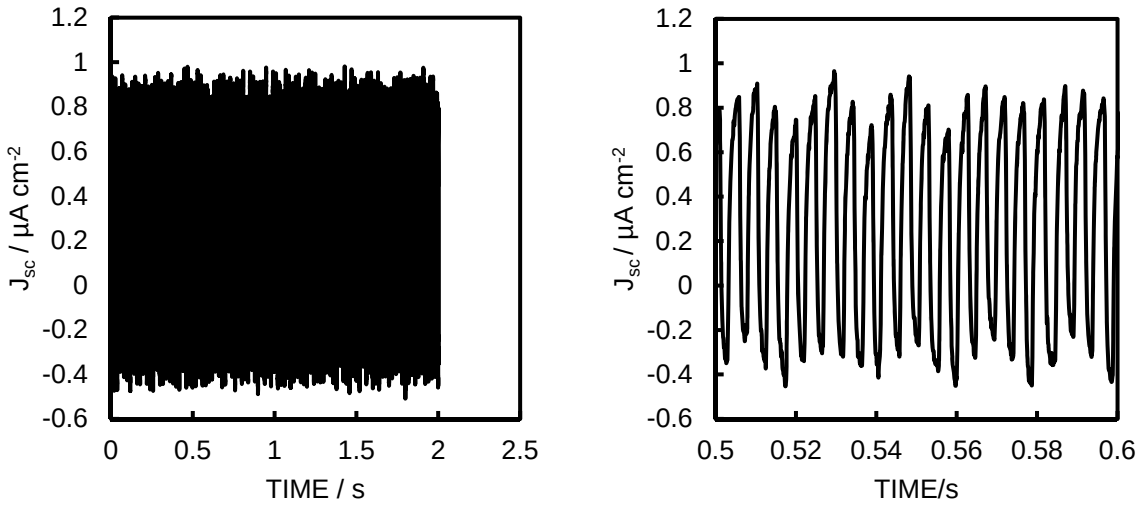

Figure S5. (left) Alternating current generation from PCET based solar cell containing 0.01 M Q/H_2Q, 0.04 M Sp1 and 0.1 M $Bu_4N^+PF_6^-$ in MeCN. One of the two ITO electrodes was illuminated with discontinuous UV light (5 mW cm^{-2}, 0.5 s) from DG-4 while the other constantly with UV. (right) Zooming from 0.5 s to 0.6 s from Fig. S4(left).