Electronic Supplementary Information

Förster Resonance Energy Transfer Enabled Photo-rechargeable Battery with an Energetically Misaligned Cu-Porphyrin Dye/Cu:V_2O_5 Photocathode

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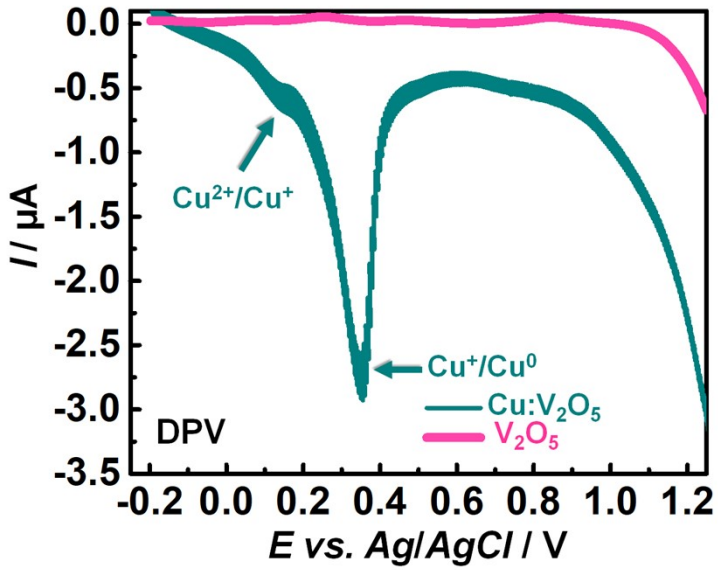

Figure S1 Differential pulse voltammetry (DPV) was performed on a Biologic SP-300 machine, where the pulse height P_H was maintained at a constant level with respect to the base potential. The record of the experiment is a plot of the current difference, $\delta I = I_f$ (current before the pulse) – I_r (current late in the pulse) versus the base potential. Typical values for the parameters are: S_t = 500 ms; S_H+P_H = 7.5 mV; pulse width = 50 ms and S_H/S_t = 2 mV/s.

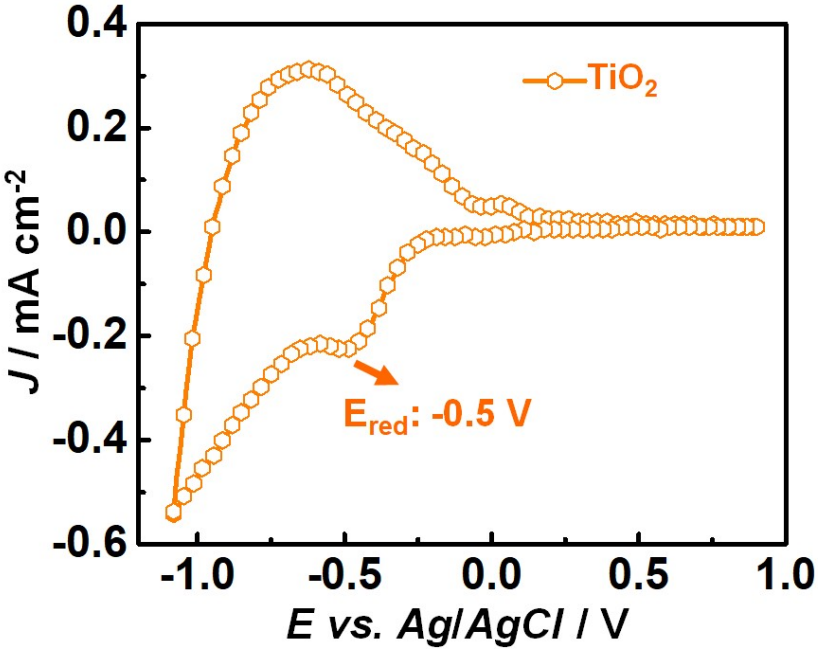

Figure S2 CV plot of a TiO_2/FTO film in a three-electrode cell with a Pt rod as a CE and Ag/AgCl/KCl as a RE in a 1 M $ZnCl_2$/γ-BL electrolyte.

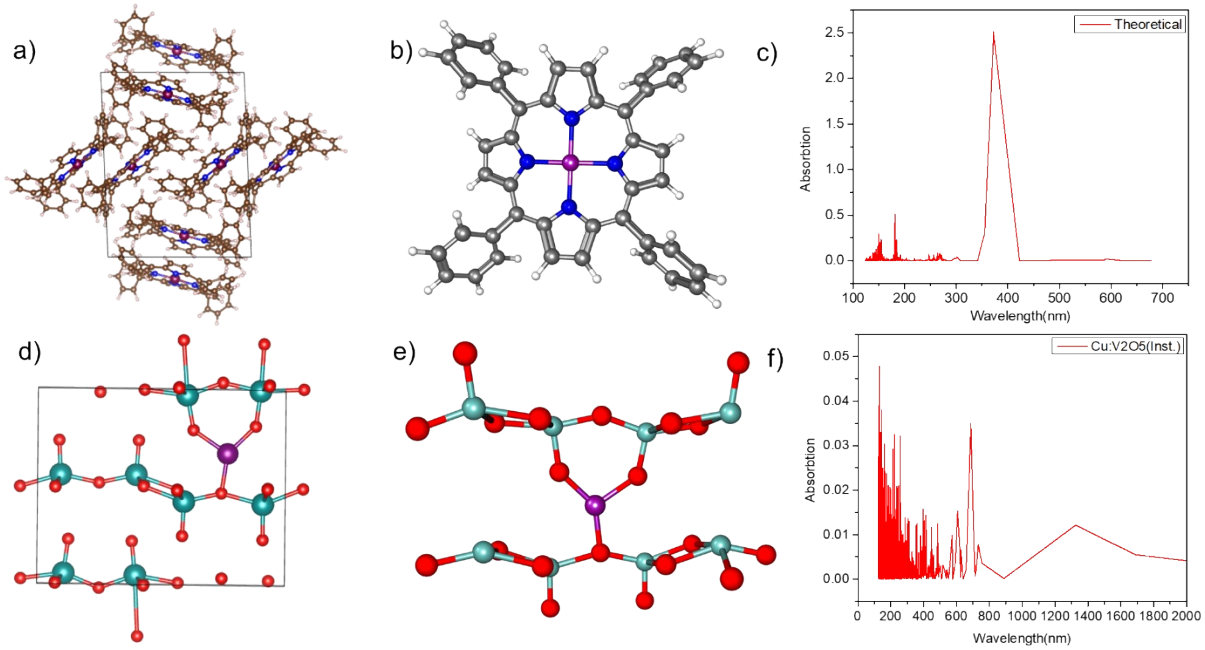

Figure S3 (a) DFT-optimised bulk structure of CuTPP, (b) Cluster Model for TD-DFT calculations and (c) TD-DFT computed absorption spectrum of CuTPP. (d) DFT-optimised bulk structure of Cu:V_2O_5, (e) Cluster Model for TD-DFT calculations and (f) TD-DFT computed absorption spectrum of Cu:V_2O_5.

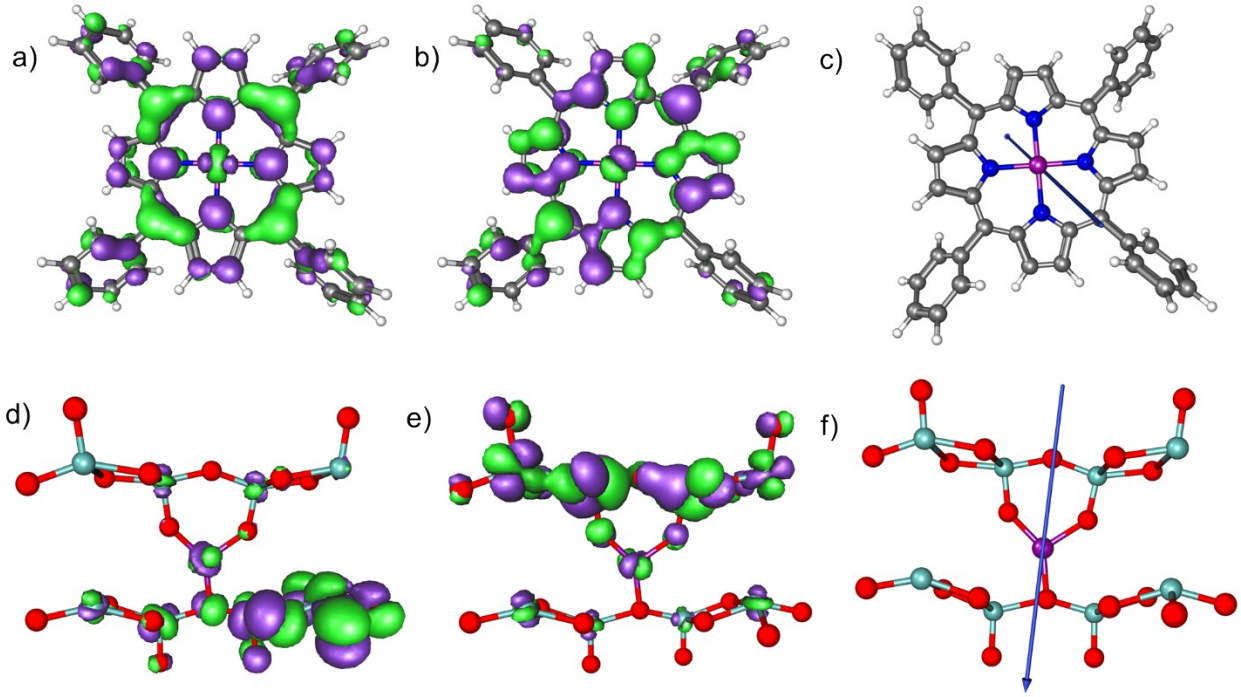

Figure S4 (a) HOMO of CuTPP, (b) LUMO of CuTPP and (c) orientation of the dipole moment of CuTPP. (d) HOMO of Cu:V_2O_5, (e) LUMO of CuV_2O_5 and (f) orientation of the dipole moment of CuV_2O_5.

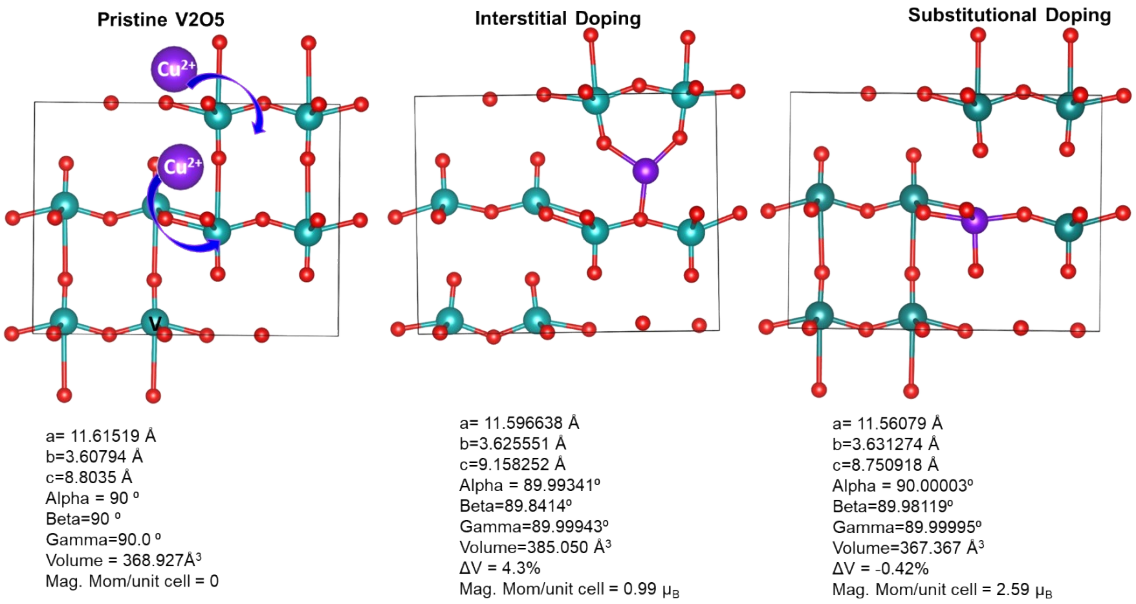

Figure S5: Periodic DFT optimized V_2O_5, interstitial doped structure and substitutional doped structure.

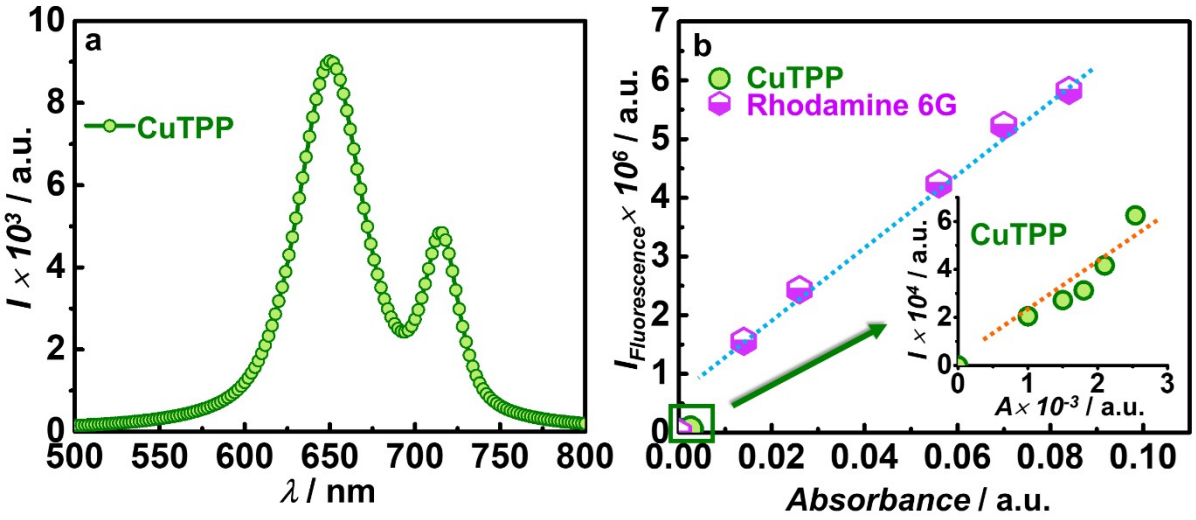

Figure S6 (a) Fluorescence spectrum and (b) quantum yield plots for CuTPP.

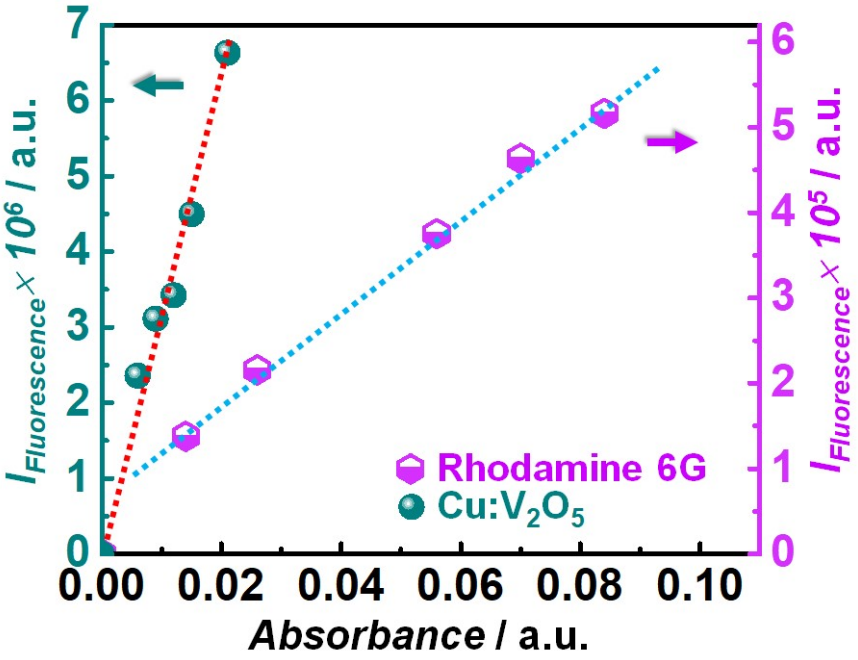

Figure S7 Integrated fluorescence intensity (obtained at λ_{ex} = 450 nm) versus absorbance of the donor (Cu:V_2O_5) and reference (Rhodamine 6G) films.

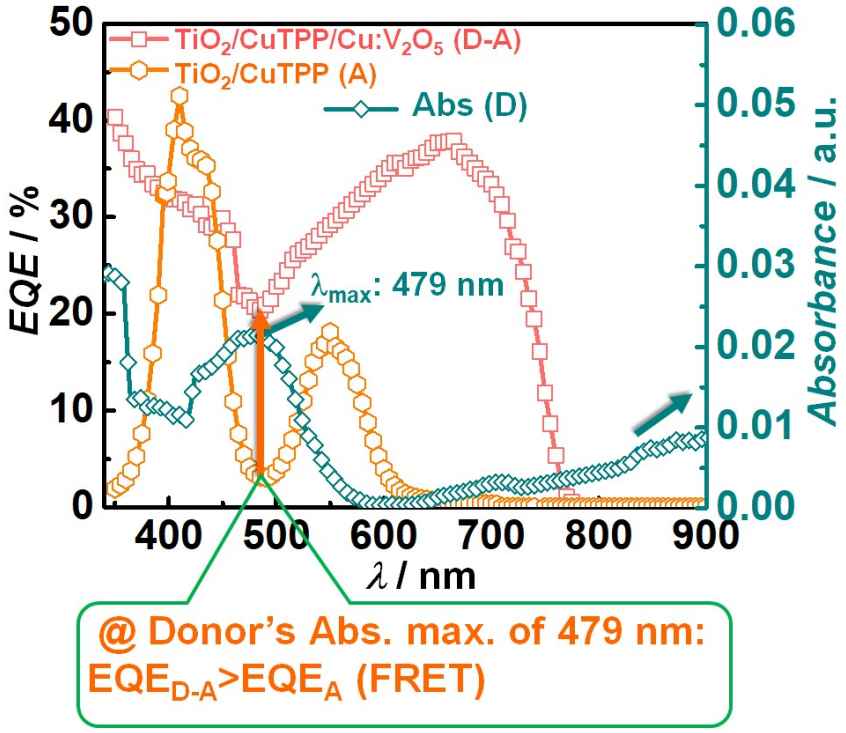

Figure S8 EQE versus wavelength plots of D-A and A-only cells and absorbance versus wavelength of donor.

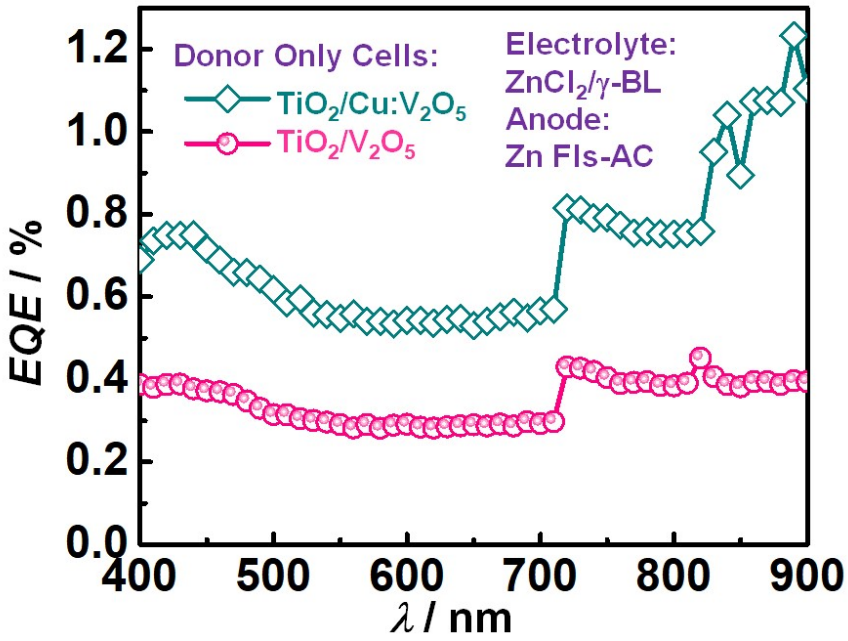

Figure S9 EQE versus wavelength plots of TiO_2/Cu:V_2O_5 and TiO_2/V_2O_5 based cells (without the acceptor, CuTPP).

Table S1 Solar cell parameters of photo-batteries with 1 M $ZnCl_2$/γ-BL electrolyte and Zn FLs-AC anode under irradiance (1 sun, 100 mW cm^{-2}, AM 1.5) based on different photocathodes.

Photocathode	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	PCE_{best} (%)	$PCE_{average}$ (%)
TiO_2/CuTPP	571	2.44	27.0	0.38	0.34±0.023
TiO_2/CuTPP/V_2O_5	1089	4.99	42.9	2.33	2.01±0.18
TiO_2/CuTPP/Cu:V_2O_5	1414	7.13	54.7	5.51	4.98±0.37

Table S2 Five cell data for photo-batteries.

TiO_2/CuTPP	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Cell-1	571	2.44	27.3	0.38
Cell-2	542	2.28	27.1	0.33
Cell-3	523	2.20	27.0	0.31
Cell-4	546	2.32	27.2	0.34
Cell-5	534	2.27	27.1	0.33
Average	543	2.30	27.1	0.34

TiO_2/CuTPP/V_2O_5	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Cell-1	1089	4.99	42.9	2.33
Cell-2	936	4.58	42.8	1.83
Cell-3	1008	4.46	42.8	1.92
Cell-4	939	4.76	42.7	1.90
Cell-5	1047	4.58	43.0	2.06
Average	1004	4.67	42.8	2.01

TiO_2/CuTPP/Cu:V_2O_5	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Cell-1	1414	7.13	54.5	5.49
Cell-2	1399	6.92	54.9	5.31
Cell-3	1360	6.64	54.6	4.93
Cell-4	1288	6.66	54.6	4.68
Cell-5	1260	6.54	54.7	4.51
Average	1344	6.78	54.7	4.98

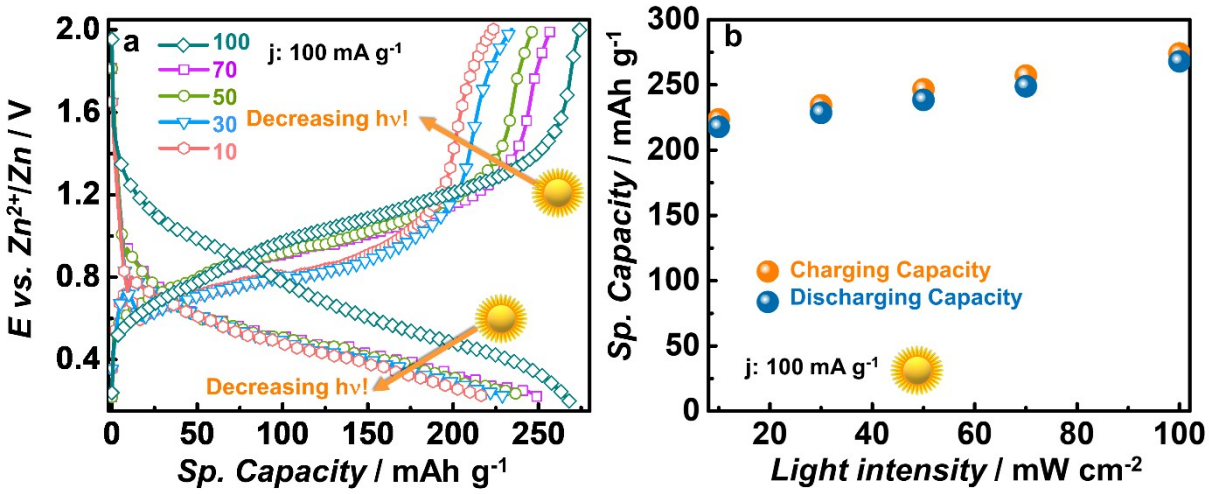

Figure S10 (a) GCD plots of the TiO_2/CuTPP/Cu:V_2O_5/Zn^{2+}/Zn Fls-AC photo-battery under varying intensities of impinging radiation. (b) Capacity versus intensity for the same cell.

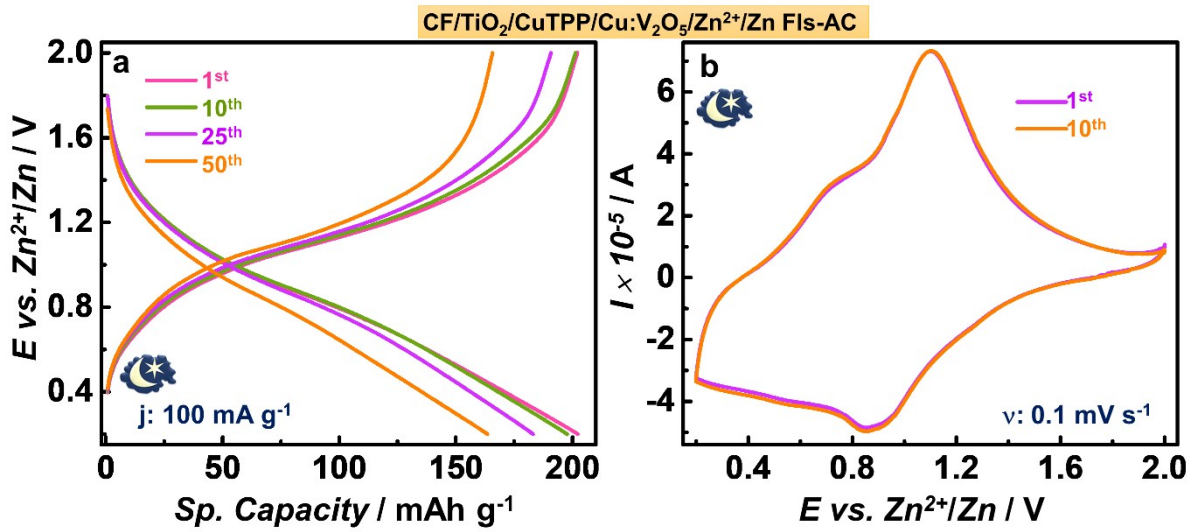

Figure S11 (a) GCD plots and (b) CV plots of the CF/TiO_2/CuTPP/Cu:V_2O_5/Zn^{2+}/Zn Fls-AC cell.

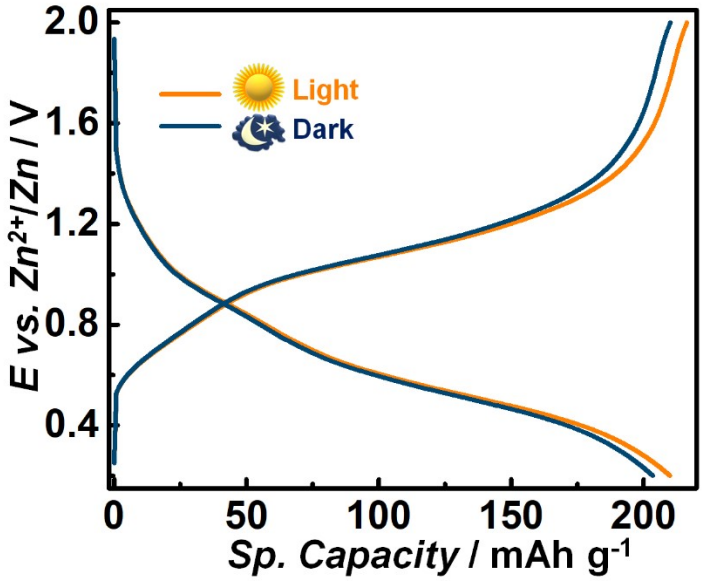

Figure S12 GCD plots of cells without CuTPP and having only Cu:V_2O_5 in dark and light under 100 mA g^{-1}.

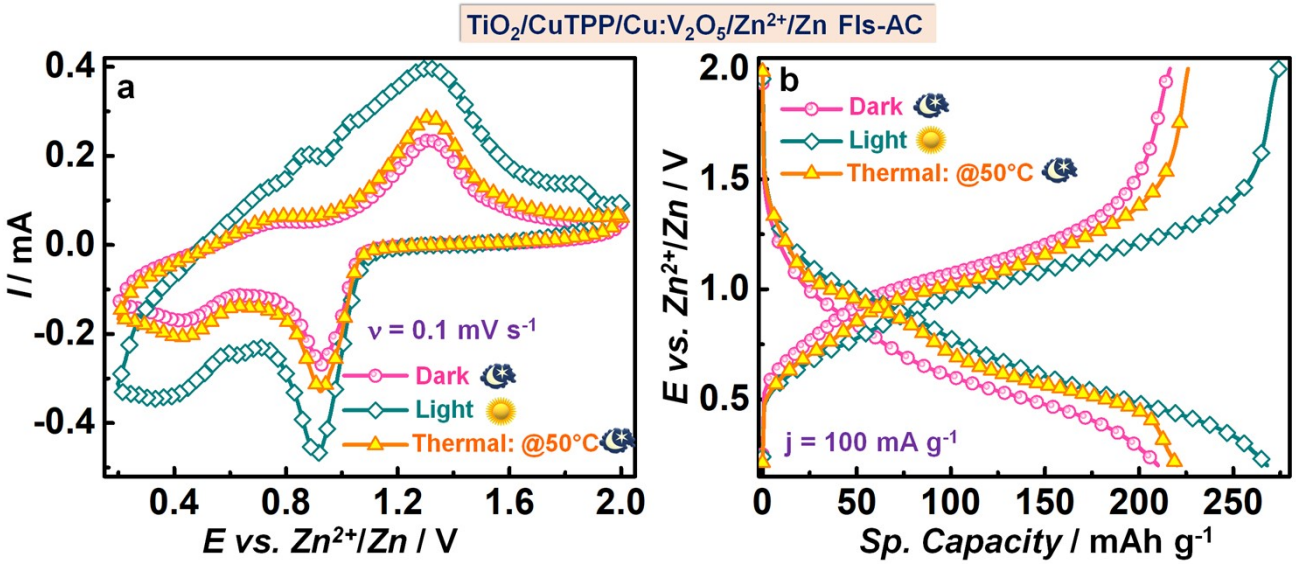

Figure S13 Comparison of CV- and GCD- plots of photo-battery in dark (at 25 °C), in dark (at 50 °C, thermal effect) and under irradiance (1 sun).

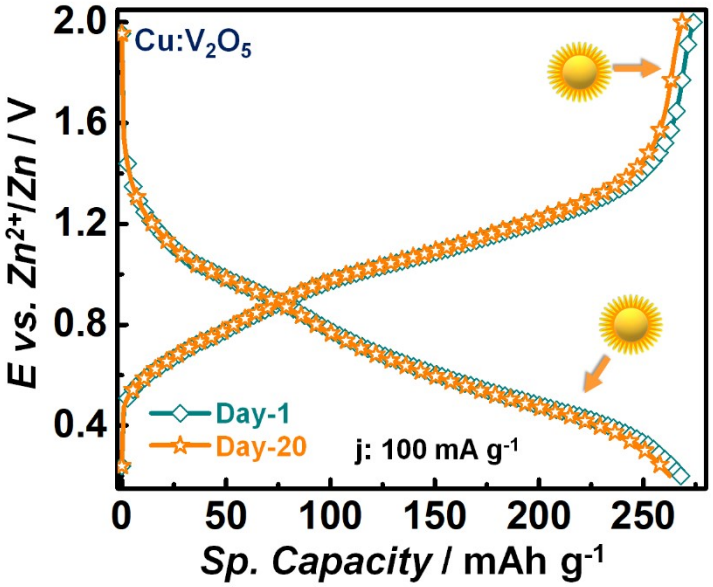

Figure S14 GCD curves recorded before and after 20 days of continuous photocharging and photo-discharge (under 1 sun + applied current density of 100 mA g^{-1}) for the TiO_2/CuTPP/Cu:V_2O_5/Zn^{2+}/Zn Fls-AC photo-battery.

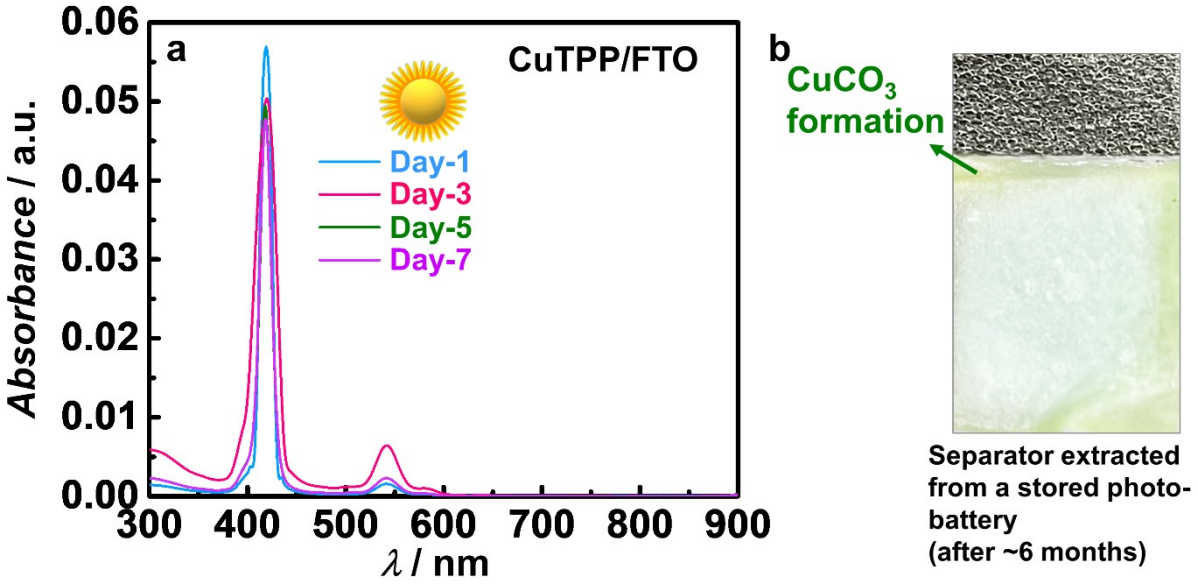

Figure S15 (a) Absorbance of a CuTPP/FTO film recorded intermittently during prolonged exposure to sunlight. (b) Photograph of a separator extracted from the photo-battery after storage for ~6 months.

Table S3 Comparison of storage and conversion performances of Zn-ion based photo-batteries from literature.

Cell configuration	Electrolyte	ΔV (V)	Specific Capacity (Dark)	Specific Capacity (Light)	PCE (%)	$\eta_{overall}$ (%)
(VO_2/ZnO@ CF//Zn Foil [6]	Aq. 3 M $Zn(CF_3SO_3)_2$	0.2-1.4	367 mAh g^{-1} at 200 mA g^{-1}	432 mAh g^{-1} at 200 mA g^{-1} and 12 mW cm^{-2} light intensity at 455 nm	0.51	--
MoS_2/ZnO@CF/ / Zn Foil [7]	Aq. 3 M $Zn(CF_3SO_3)_2$	0.2-1.2	245 mAh g^{-1} at 100 mA g^{-1}	340 mAh g^{-1} at 100 mA g^{-1} and 12 mW cm^{-2} light intensity at 455 nm	1.8	--
VO_2/ZnO@CF// Zn Foil [8]	Aq. 3 M $Zn(CF_3SO_3)_2$	0.2-1.4	282 mAh g^{-1} at 200 mA g^{-1}	315 mAh g^{-1} at 200 mA g^{-1} and 12 mW cm^{-2} light intensity at 455 nm	0.18	--
P3HT/V_2O_5/rGO @CF//Zn Foil [9]	Aq. 3 M $Zn(CF_3SO_3)_2$	0.2-1.6	190 mAh g^{-1} at 50 mA g^{-1}	370 mAh g^{-1} at 50 mA g^{-1} and 12 mW cm^{-2} light intensity at 455 nm	1.2	--
FTO/TiO_2/CuTPP/V_2O_5//Zn Fls-AC/Ni Foam (This Work)	1 M $ZnCl_2$ in γ-BL	0.2-2.0	120 mAh g^{-1} at 100 mA g^{-1}	150 mAh g^{-1} at 100 mA g^{-1} and 1 sun (100 mW cm^{-2})	2.33	3.3
FTO/TiO_2/CuTPP/Cu:V_2O_5//Zn Fls/Ni Foam (This Work)	1 M $ZnCl_2$ in γ-BL	0.2-2.0	210 mAh g^{-1} at 100 mA g^{-1}	268 mAh g^{-1} at 100 mA g^{-1} and 1 sun (100 mW cm^{-2})	5.51	3.9

CF: Carbon Felt, Aq.: Aqueous, γ-BL: γ-Butyrolactone

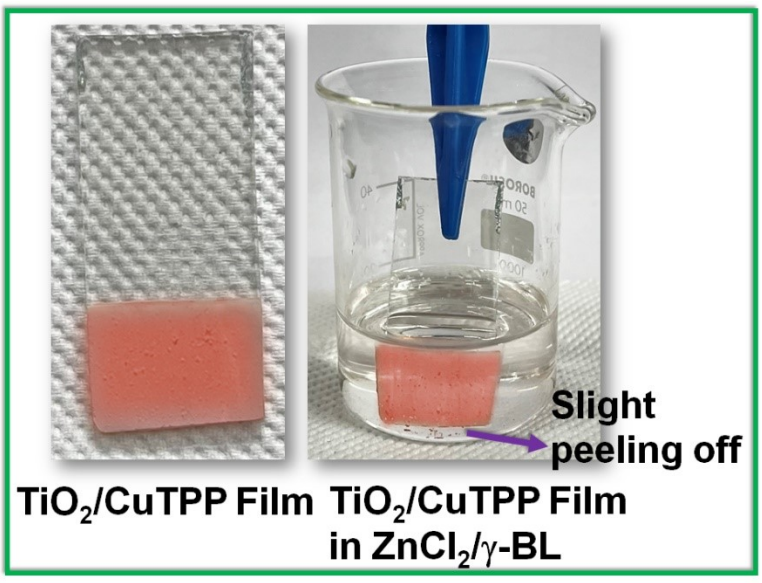

Figure S16 Photographs of a TiO_2/CuTPP film immersed in the electrolyte: 1 M $ZnCl_2$/γ-BL, showing its good stability.

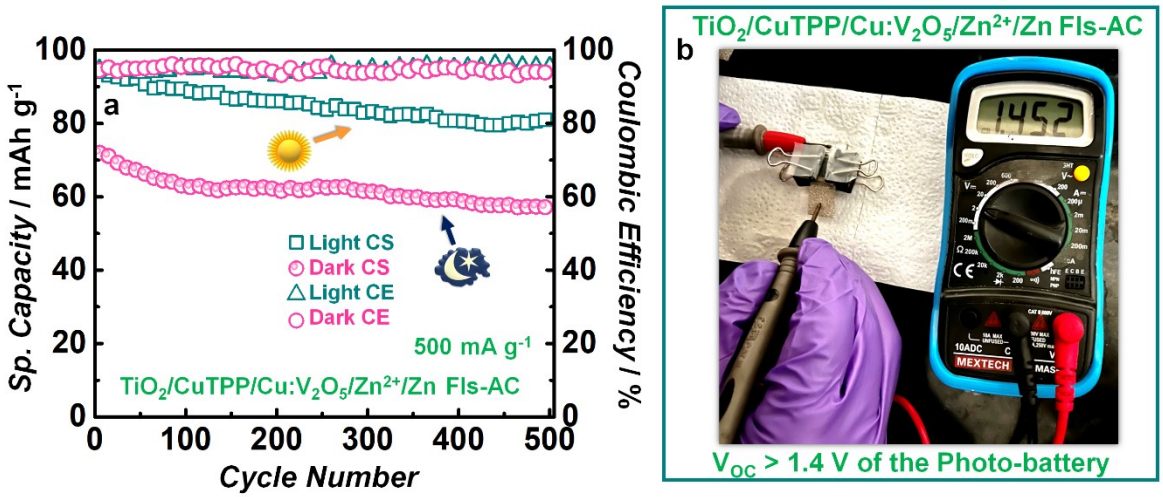

Figure S17 (a) Photograph of a photo-charged TiO_2/CuTPP/Cu:V_2O_5/Zn^{2+}/Zn Fls-AC photo-battery and (b) cycling stability over 500 charge-discharge cycles, at 500 mA g^{-1}, in light (1 sun) and in dark.

Table S4 Fitted parameters of the Nyquist plots for TiO_2/CuTPP/Oxide/Zn^{2+}/Zn Fls-AC photo-batteries in dark and light (1 sun, 100 mW cm^{-2} irradiance).

Cell configuration	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	Y_o (mS $s^{1/2}$ cm^{-2})
V_2O_5 (Dark)	46.0	3643.7	0.4	0.6
V_2O_5 (Light)	44.0	1863.2	0.3	2.1
Cu:V_2O_5 (Dark)	43.4	5.5	4.5	5.0
Cu:V_2O_5 (Light)	41.5	7.2	0.3	9.4
TiO_2/Cu:V_2O_5/Zn^{2+}/Zn Fls-AC (1 sun, 100 mW cm^{-2} irradiance):				
TiO_2/Cu:V_2O_5/Zn^{2+}/Zn Fls-AC (Light):				
Donor Only Cell	51.0	51.5	430	----

Calculation of overall photoconversion and storage efficiencies ($\eta_{overall}$):

$\eta_{overall} = E_{battery} \times A_{battery} \times 100 / P_{light} \times t_{charging} \times A_{solar}$

In the above equation, $E_{battery}$ is the energy density of the photo-battery in W s cm^{-2}, obtained from the capacity corresponding to full discharge to 0 V in dark under an applied current density (j = 180 mA g^{-1}) when photocharged under 1 sun irradiance to a given voltage under no applied bias or current in the preceding cycle. Here, $\Delta V_{(dark\ discharge)}$ values are 1.2 V and 1.4 V respectively for the TiO_2/CuTPP/V_2O_5/Zn^{2+}/Zn Fls-AC and the TiO_2/CuTPP/Cu:V_2O_5/Zn^{2+}/Zn Fls-AC photo-batteries. The active electrode areas ($A_{battery}$ and A_{solar}) are 0.5 cm^2 each and P_{light} was taken as 100×10^{-3} W cm^{-2}. The time required to photo-charge the photo-batteries to 1.2

and 1.4 V respectively without the application of any I or V, under 1 sun irrdiance is $t_{charging}$, and $t_{charging}$ = 380.8 s and 163.6 s for Cu:V_2O_5 and V_2O_5 respectively.

The energy density is calculated using the following equation.

$$E_{battery} = \frac{1}{m}\int_0^t Vidt$$

In the above equation, 'm' is the active mass loading, 'i' is the applied current during dark discharge, $V\int_0^t dt$ is the integrated area in the voltage-time plot. The energy densities were calculated to be 1.48 and 0.55 W s cm^{-2} for the photo-batteries with Cu:V_2O_5 and V_2O_5 respectively, from the data shown in Figure 7a. Using these values, the $\eta_{overall}$ values were estimated to be 3.9% and 3.3% respectively.

Scheme S1 Schematic showing step-wise synthesis of (a) V_2O_5 and Cu:V_2O_5 and (b) CuTPP dye.