# **Supporting Information**

# Unlocking High-Performance Photocapacitors for Edge Computing in Low-Light Environments

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#### S1 Experimental section

**Materials** Unless otherwise specified, all compounds and solvents were obtained from Sigma-Aldrich and were utilized as received, without undergoing any additional purification. The purity of the solvents utilized in electrochemistry and spectroscopy was 99.9%.

**Synthesis of polyviologens** PV1 and PVN were synthesized via the Zincke reaction. Although a Sephadex LH20 column was employed to remove short-chain impurities, their limited solubility in both organic and aqueous solvents (being highly soluble only in MeOH) rendered further purification unnecessary.

**Synthesis of Zinke salt, bis-[1,1'-(2,4- dinitrophenyl-4,4'-bipyridinium dichloride**)] The procedured described by Beladi et. al was followed.<sup>1</sup> 40 mmol (6.4 g) of 4,4-bipyridine was reacted with 140 mmol (28 g) of 1-chloro-2,4-dinitrobenzene. The reaction was refluxed in MeCN at 80 °C during 72 h. The pale yellow precipitate was filtered and washed with MeCN and several times with acetome. The product was vacuum-dried and used as is for the synthesis of PV1 and PVN.



Figure S1: Zincke reaction

**Synthesis of PV1** A total of 0.8 mmol (0.45 g) of bis-[1,1'-(2,4-dinitrophenyl-4,4'-bipyridinium dichloride)] and 0.8 mmol (0.1698 g) 4,4'- ethylenedianiline were dissolved in methanol/water (8/2) and refluxed for two weeks. Afterward, the solvent was evaporated, and the solid residue was dispersed in acetone and refluxed for an additional 18 hours. The resulting precipitates were filtered and washed with acetone. The yellow powder obtained was fractionated using a Sephadex LH20 column and analyzed by <sup>1</sup>H-NMR.



Figure S2: PV1 synthesis

**Synthesis of PVN** A mixture of 0.8 mmol (0.45 g) of bis-[1,1'-(2,4- dinitrophenyl-4,4'-bipyridinium dichloride)] and 0.8 mmol (0.29 g) 4,4'-(1,1'-Biphenyl-4,4'-diyldioxy)dianiline together with 35 mL of EtOH were refluxed for two weeks. After evaporating the solvent, the solid residue was dispersed in acetone and refluxed for 18 hours. The precipitate was filtered, washed with acetone, and the resulting brown powder was fractionated using a Sephadex LH20 column, followed by analysis via<sup>1</sup>H-NMR.



Figure S3: PVN synthesis

**Development of Chitosan-based membranes** Chitosan-based membranes were produced following a procedure adapted from <sup>2,3</sup>. Briefly, 1.5 g of Chitosan (medium molecular weight, 75-85% deacetylated, Sigma-Aldrich) was dissolved in 100 mL of 1% (v/v) acetic acid solution. The solution was stirred at room temperature for 2 hours to ensure complete dissolution. Subsequently, the solution was filtered through a glass filter to remove any undissolved particles. The filtered Chitosan solution was then cast onto Teflon plates and allowed to dry at room temperature for 48 hours. The formed membranes were neutralized by immersion in 1 M NaOH solution for 30 minutes, followed by thorough washing with distilled water until neutral pH was achieved. The neutralized membranes were then dried at room temperature for 24 hours. Prior to use in the photocapacitor devices, the Chitosan membranes were cut to the appropriate size and preconditioned at 53% relative humidity for 48 hours using a saturated magnesium nitrate solution. This preconditioning step ensures consistent moisture content and mechanical properties of the membranes. The Chitosan membranes prepared by this method have been shown to have good mechanical properties, with tensile strength around 45 MPa and elongation at break around 15% <sup>3</sup>. Their porous structure

and positive charge make them suitable as separators in the photocapacitor devices, allowing ion transport while preventing short circuits between electrodes.

**Electrochemical measurements** Cyclic voltammetry measurements were performed with a potentiostat/galvanostat AUT 71326 Metrohm/Autolab in a three-electrode setup cell. A glassy carbon electrode served as the working electrode (0.07 cm2 area) and a graphite rod as the counter electrode; a non-aqueous reference electrode of Ag/AgCl (1 M LiCl in DIW) was used, with an intermediate bridge tube containing the same supporting electrolyte as the working electrode compartment.

**Fabrication of photovoltaic cells** A a  $TiO_2$  layer was deposited on cleaned Nippon sheet glass (Pilkington, St. Helens, UK), with a sheet resistance of 10 ohm/square via spray pyrolysis using a 0.2 M titanium bis(isopropoxide) bis(acetylacetonate) solution in isopropanol at 450 °C. TiO<sub>2</sub> anodes of 0.384 cm<sup>2</sup> (7 mm diameter circles) were screen-printed (Seritec Services SA, Corseaux, Switzerland) using DSL 30 NRD-T TiO<sub>2</sub> paste (4 µm)(Dyesol/GreatCellSolar, Queanbeyan, Australia) colloidal (30 nm). The samples were dried at 120 °C, and a scattering layer was screenprinted on top of the mesoporous film (4 µm) (Dyesol/GreatCellSolar WER2-0, 400 nm), gradually heated to 500 °C and sintered for 30 minutes. The substrates underwent a post-treatment with a 13 mM aqueous TiCl<sub>4</sub> solution for 30 min at 70 °C and sintered at 450 °C for 30 min. After cooling, the substrates were immersed in a dye solution containing 0.5 mM L1 dye in acetonitrile 1:1 tert-butanol, and 0.1 mM XY1, 5 mM chenodeoxycholic acid in chloroform 3:7 ethanol for 24 hours (both dyes from Dyenamo, Stockholm, Sweden). PEDOT counter electrodes were electro-polymerized from a 0.01 M aqueous solution of 3,4-ethylenedioxythiophene with 0.1 M sodium dodecyl sulphate as a surfactant. The redox electrolyte contained 0.2 M Cu(tmby)<sub>2</sub> TFSI and 0.06 M Cu(tmby)<sub>2</sub> TFSI<sub>2</sub> (both from Dyenamo), 0.1 M lithium bis(trifluoromethanesulfonyl) imide and 0.6 M N-methyl benzimidazole in acetonitrile. The DSCs were sealed using ThreeBond 3035B UV glue (Düsseldorf, Germany) and cured with a CS2010 UV source (Thorlabs, Newton, NJ, USA). The electrolyte was injected through a hole in the counter electrode, which was then sealed with additional UV glue.

**Fabrication of photocapacitors** A PEDOT substrate of 4.2 cm<sup>2</sup> was employed as a common electrode for the photovoltaic and supercapacitor unit. The polyviologen material was dropcasted on the left-hand side of the PEDOT substrate at 70 °C and annealed at 100 °C for 10 min. After cooling, the DSC was ensembled on the right-hand side of the substrate following the procedure mentioned above. Carbon substrates of 50  $\mu$ m and 0.8 cm<sup>2</sup> were screen-printed employing the low-annealing temperature paste from Dyenamo. An aqueous electrolyte of KCl 1.5M with 3 mg mL<sup>-1</sup> NaAlg as a binder was deposited on top of the polyviologen and the carbon. The Chitosan or Nafion membrane was stacked on top of the substrates, and the supercapacitor side was sealed with ThreeBond (Düsseldorf, Germany) 3035B UV glue.

**Characterization of photocapacitors** Current-voltage measurements under AM 1.5G illumination were carried out in ambient air using a Wavelabs SINUS-70 ADVANCED LED Solar Simulator. An X200 source meter (Ossila, Sheffield, UK) was used to assess the solar cell performance (scan speed 5 mV s<sup>-1</sup>). A circular mask was employed to confine the active solar cell area to 0.196 cm<sup>2</sup>. Ambient light characterization was carried out with a Warm White 930 18 W florescent tube (OSRAM,Munich, Germany). The lamp spectrum is shown in Fig. S36. A detailed description of the assessment of ambient or indoor light sources, their calibration, and the conversion of emission spectra, illuminance and power density is provided in our recent article.<sup>4</sup> The stabilized light intensity was calibrated with a spectroradiometer. The photocharging process was monitored with an Autolab potentiostat with a galvanostatic charge-discharge program. A negative current of 1 A was first applied for 10 s to guarantee that the photocapacitor was discharged before turning the light on. When the light is turned on, photocharging was performed for 3 min for both small and big cells. The light is turned off for the dark discharge, and the photocapacitors are kept under dark conditions to prevent light-charging.

**Electrochemical impedance** Electrochemical impedance spectra were recorded using a PGSTAT12 potentiostat (Autolab) in the frequency range from 1 MHz to 0.01 Hz, with a 10 mV sinusoidal AC perturbation, at different DC bias potentials (from 1.0 V to 0). All measurements were carried at 20 °C. The resulting Nyquist plots were analyzed with Z-View software (Scribner Associates Inc.)

and fitted employing the equivalent circuit shown in Fig. S18a.

**Computational details** Density Functional Theory (DFT) calculations were performed with Gaussian 16.<sup>5</sup> Structural optimizations, molecular frequencies, and thermochemistry data were obtained at the PBE0 level of theory,<sup>6</sup> including Grimme's dispersion correction D3 with the Becke-Johnson damping function.<sup>7</sup> The water solvent was considered with the polarizable continuum model (PCM).<sup>8</sup> The 6-31++G(d,p) basis set was used for C, N, H and O atoms. The default maximum force and displacement tolerance parameters in Gaussian were considered for the ground-state minimum-energy structures. Molecular frequencies were computed within the harmonic oscillator approximation, and the thermochemical data were computed at room temperature (298 K). The absorption wavelengths ( $\lambda_{cal}$ ) of PV compounds were computed via the TD-DFT. Internal reorganization energies in solution.  $\lambda_r$  was evaluated in the gas phase as the electronic energy differences of PV at the relaxed geometries that correspond to the initial and final electronic states. We also calculated the redox potential ( $E_r$ ) of PV reduction in solution with the following formula:<sup>9,10</sup>

$$E_r(\text{vs NHE}) = -\frac{\Delta G_r}{nF} - 4.43 \text{ V}$$
(1)

where  $\Delta G_r$  is the free energy change of the reduction half-reaction in solution, n is the number of electrons transferred (n = 1) and F is the Faraday constant (which simplifies to 1 eV V<sup>-1</sup> in this context), the -4.43 V is the potential of the electrons relative to the vacuum for the normal hydrogen electrode (NHE). We refer the  $E_r$  to Ag/AgCl electrode, thus we subtract the redox potential of such an electrode vs NHE (-0.197 V).

**IoT Characterization and benchmarking** Two distinct network topologies were implemented and benchmarked as outlined in Fig. 4.: a) a single-layer star-topology with each IoT node on layer 1 (L1) sending data to a mains-powered fog node (L0) and b) a three-layer tree-topology with two branches, each branch aggregating and computing data from the third layer (L3) up to the fog node (L0). The purpose of the star-topology was implemented and benchmarked for 24 hours at 1000 lx to ensure equivalent performance of the IoT devices under similar environmental conditions. The IoT devices employed PID-controlled intermittent sleep based on the voltage of a buffer capacitor, to maintain a balance between energy consumption (including leakage) and the harvested and stored energy. The performance using the photocapacitors was compared to an IoT sensor powered by commercially available Powerfilm LL200-4.8-3.7, thin-film amorphous silicon flexible indoor light harvesting modules. The dimensions of the LL200-4.8-3.7 are 9.4 cm  $\times$  3.65 cm with a (measured) active area of 3.3 cm  $\times$  7.8 cm, thus 25.74 cm<sup>2</sup>. The PC IoT nodes were powered by 6 PC modules with an active area of 4.2 cm<sup>2</sup> per PC, with a total active area of 25.2 cm<sup>2</sup>. The IoT system powered by the high-voltage photocapacitors (with PVN) significantly outperformed the modules in the single-layer star topology, transmitting an average of 3.4 data packages per second compared to 1.5 packages per second for the Powerfilm-powered devices. The three-layer tree topology showed and even larger performance improvement for the photocapacitors, around 3.5 times better than the commercial modules, with 137 vs. 39 aggregated MNIST predictions (1.90 predictions per hour vs. 0.54 predictions per hour) at 1000 lx and 7 vs. 2 aggregated MNIST predictions at 250 lx (0.1 pred/h vs. 0.03 pred/h, respectively). These results highlight the superior performance of photocapacitor-powered IoT nodes, particularly in multi-layered network configurations.

## S2 Structural Characterisation

This section presents the molecular structures and NMR spectra of PV1 and PVN polyviologens. These characterizations confirm the successful synthesis and purity of the materials used in our photocapacitors. **PV1:** <sup>1</sup>H NMR (400 MHz, MeOD):  $\delta$  9.46 (d, J = 6.8 Hz, 4H, bipyridinium-H), 8.88 (d, J = 6.8 Hz, 4H, bipyridinium-H), 7.72 (d, J = 8.4 Hz, 4H, phenyl-H), 7.08 (d, J = 8.4 Hz, 4H, phenyl-H), 4.75 (s, 4H, -CH<sub>2</sub>-), 3.25 (s, 4H, -NH<sub>2</sub>). **PVN:** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta$  9.10 (d, J = 6.8 Hz, 4H, bipyridinium-H), 8.85 (d, J = 6.8 Hz, 4H, bipyridinium-H), 7.70 (d, J = 8.8 Hz, 4H, phenyl-H), 7.35 (d, J = 8.8 Hz, 4H, phenyl-H), 7.12 (d, J = 8.8 Hz, 4H, phenyl-H), 6.92 (d, J = 8.8 Hz, 4H, phenyl-H), 3.75 (s, 3H, -O-C-H), 3.58 (s, 4H, -NH<sub>2</sub>). The peak at 4.70 can be assigned to residual water in the sample.



Figure S4: Molecular structure and <sup>1</sup>H NMR spectrum of PV1

In both spectra the distinctive peaks correlate with their chemical structure. The characteristic signals of the bipyridinium protons are observed in the downfield region ( $\delta$  9.46–8.8 ppm for PV1 and  $\delta$  9.10–8.85 ppm for PVN), corresponding to highly deshielded protons, in the aromatic rings directly adjacent to electron-withdrawing groups, such as the nitrogen atoms in the viologen core, indicating the successful formation of the viologen structure.

These peaks at 8.88 for PV1 and 8.85 for PVN can be assigned to aromatic protons in an electronpoor environment, close to quaternary nitrogen centers (viologen rings).

The phenyl protons appear in the aromatic region ( $\delta$  7.72–7.08 ppm for PV1 and  $\delta$  7.70–6.92 ppm for PVN). In PVN the additional set of peaks corresponds to aromatic protons on the viologen ring and adjacent functional groups. These additional peaks in PVN can be linked to the differences in



Figure S5: Molecular structure and <sup>1</sup>H NMR spectrum of PVN

structure between PVN and PV1, specifically accounting for extra substituents or polymeric units present in PVN. In PV1 the presence of the -CH<sub>2</sub>- linker is confirmed by the singlet at  $\delta$  4.75 ppm, while the signal for the -NH<sub>2</sub> groups appears at $\delta$  3.28 ppm coming from the monomer. The molecular weight distribution and polydispersity index (PDI) for PVN were determined using complementary <sup>1</sup>H NMR spectroscopy and mass spectrometry (LC-MS). From the NMR spec-

complementary <sup>1</sup>H NMR spectroscopy and mass spectrometry (LC-MS). From the NMR spectrum, integration of repeating unit signals (bipyridinium and phenyl protons at  $\delta$  9.10–6.92 ppm) relative to the end-group signals (methoxy at  $\delta$  3.75 ppm and amino at  $\delta$  3.58 ppm) yielded a degree of polymerization (DP) of approximately 8, corresponding to a number-average molecular

weight  $(M_n)$  of about 3947 g mol<sup>-1</sup> (486.09 g mol<sup>-1</sup> per repeating unit plus 58.12 g mol<sup>-1</sup> for end-groups). LC-MS analysis revealed a comprehensive mass distribution from m/z 113 to 1100,



Figure S6: ESI-MS spectrum of PVN (Peak 4, RT = 1.633-1.999 min) showing m/z distribution 113-1100. NL = 9.063E03.

with significant peaks observed at m/z 482 (94%), 532 (100%), 597 (106%), 683 (121%), 785 (137%), 913 (161%), 971 (171%), and 1100 (194%). Explicit calculation from these MS abundances provided a  $M_n = 812.3$  g mol<sup>-1</sup>, a  $M_w = 859.5$  g mol<sup>-1</sup>, and a PDI =  $M_w/M_n = 1.058$ . The observed difference between NMR and MS-derived molecular weights is attributed to known limitations of MS detection for higher molecular weight oligomers. These values confirm a narrow molecular weight distribution aligning with the observed clean NMR spectra and excellent electrochemical stability.

#### S3 Electrochemical Characterization

This section details the electrochemical properties of our polyviologen compounds. We present cyclic voltammetry to elucidate the redox behavior and capacitive properties of the materials. CVs in solution: WE: glassy carbon, RE: Ag/AgCl, CE: Pt wire

Table S1: Oxidation and reduction peaks from cyclic voltammetry in aqueous solutions with 0.1 M KCl as supporting electrolyte or deposited on FTO.

PV	OX1 (V vs	RD1 (V vs	E01 (V vs	OX2 (V vs	R2 (V vs	E02 (V vs
	Ag/AgCl)	Ag/AgCl)	Ag/AgCl)	Ag/AgCl)	Ag/AgCl)	Ag/AgCl)
PV1 Solution	-0.3	-0.315	-0.3075	-0.45	-0.67	-0.56
PV1 FTO	-0.09	-0.3	-0.195	-0.29	-0.65	-0.47
PVN Solution	-0.156	-0.275	-0.2155	-0.397	-0.68	-0.5385
PVN FTO	-0.129	-0.32	-0.2245	-0.393	-0.73	-0.5615

CVs on electrodes: WE: FTO+PV, RE: Ag/AgCl, CE: Pt wire



Figure S7: Cyclic voltammograms for a) PV1 and b) PVN deposited as films on FTO electrodes as WE, 0.1 M KCl as supporting electrolyte and Pt wire as CE, carried in MeOH.

# S4 Capacitance Measurements

Here, we provide comprehensive capacitance measurements of our supercapacitor samples. The data includes galvanostatic charge/discharge measurements, cyclic voltammetry, and Electrochem-

ical Impedance Spectroscopy (EIS) offering a complete picture of the devices' capacitive performance.



Figure S8: Voltage vs time galvanostatic charge/discharge measurements of four identical supercapacitor samples containing PV1, Chitosan membrane and carbon



Figure S9: Voltage vs time galvanostatic charge/discharge measurements of four identical supercapacitor samples containing PV1, nafion membrane and carbon



Figure S10: Voltage vs time galvanostatic charge/discharge measurements of four identical supercapacitor samples containing PVN, Chitosan membrane and carbon



Figure S11: Voltage vs time galvanostatic charge/discharge measurements of four identical supercapacitor samples containing PVN, nafion membrane and carbon



Figure S12: Capacitance vs discharge current for supercapacitor samples: a) PV1//CH//C, b) PVN//CH//C, c) PV1//N//C and d) PVN//N//C



Figure S13: Cyclic voltammetry of supercapacitor samples containing PV1, chitosan membrane and carbon



Figure S14: Cyclic voltammetry of supercapacitor samples containing PV1, nafion membrane and carbon



Figure S15: Cyclic voltammetry of supercapacitor samples containing PVN, chitosan membrane and carbon



Figure S16: Cyclic voltammetry of supercapacitor samples containing PVN, nafion membrane and carbon



Figure S17: Box plots with statistics of the capacitance obtained from 4 supercapacitor samples of each condition: a) PV1//CH//C, b) PVN//CH//C, c) PV1//N//C and d) PVN//N//C



Figure S18: Electrochemical Impedance Spectroscopy (EIS) measurements of supercapacitors with polyviologen materials. a) equivalent circuit, b) PV1//CH//C, c) PV1//N//C, d) PVN//CH//C and e) PVN//N//C

# **S5** Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) images of chitosan-based membranes are presented here. These images provide insight into the membrane's morphology and structure, crucial for understanding its performance in photocapacitor devices.



Figure S19: Chitosan-based membrane SEM image at magnification 68x



Figure S20: Chitosan-based membrane SEM image at magnification 65x



Figure S21: Chitosan-based membrane SEM image at magnification 62x



Figure S22: Chitosan-based membrane SEM image at magnification 57x



Figure S23: Nafion-based membrane SEM image at magnification 47x



Figure S24: Nafion-based membrane SEM image at magnification 167x

## S6 Computational Modeling

The following figures present the results of our computational modeling studies on the PV1 and PVN polyviologen compounds, including molecular orbital distributions, IR spectra, and molecular orbital energy levels. Figure S25 presents the computed IR spectra for the PV1 and PVN



Figure S25: Computed IR spectra for monomer ( $[PV]_1$ ), dimer ( $[PV]_2$ ), and trimer ( $[PV]_3$ ) derivatives of PV1 (top), PVN<sub>U</sub> (bottom left), and PVN<sub>V</sub> (bottom right). The spectra show consistent patterns across different oligomeric states, indicating stable electronic properties.

compounds in their monomer, dimer, and trimer forms. The consistent spectral patterns across oligomeric states suggest structural stability upon polymerization. Key vibrational modes can be identified and correlated with specific structural features of the molecules. Figure S26 illustrates the spatial distribution of HOMOs and LUMOs for PV1,  $PVN_U$ , and  $PVN_V$  compounds in their various oligomeric forms. The HOMOs are primarily localized on the benzene and benzenediol rings, while the LUMOs are distributed mainly on the bipyridyl groups. This spatial separation of electron density in the frontier orbitals suggests a potential for intramolecular charge transfer, which is crucial for the compounds' electrochemical properties. Figure S27 shows the molecular



Figure S26: HOMO and LUMO distributions for PV1,  $PVN_U$ , and  $PVN_V$  compounds in their monomer ( $[PV]_1$ ), dimer ( $[PV]_2$ ), and trimer ( $[PV]_3$ ) forms. The energy values (E) for each orbital are provided in electron volts (eV). Note the localization of HOMOs primarily on the benzene and benzenediol rings, while LUMOs are distributed mainly on the bipyridyl groups.



Figure S27: Molecular orbital (MO) energy levels for monomer ( $[PV]_1$ ), dimer ( $[PV]_2$ ), and trimer ( $[PV]_3$ ) derivatives of PV1 (left), PVN<sub>U</sub> (center), and PVN<sub>V</sub> (right). The plots demonstrate the evolution of electronic structure upon oligomerization, with multiple occupied and unoccupied states appearing close in energy.

orbital energy levels for PV1, PVN<sub>U</sub>, and PVN<sub>V</sub> in their various oligomeric forms. The increasing density of states near the HOMO-LUMO gap as oligomerization progresses indicates the development of band-like electronic structure. This evolution of the electronic structure provides insight into the compounds' behavior in electrochemical applications and their potential for charge storage and transport. Table S5-S7 list the internal reorganization energies ( $\lambda_r$ ) and reductive potentials ( $E_r$  in eq. 6). Both viologens exhibit low internal reorganization energies (0.1-0.2 eV) and reductive potentials that align well with experimental data (Table S1). Collectively, these computational results provide a comprehensive view of the structural, vibrational, and electronic properties of the PV1 and PVN polyviologen compounds. The consistent patterns in MO distributions, IR spectra, and the evolution of MO energy levels demonstrate the changes that occur during oligomerization, offering valuable insights into the behavior of these materials in electrochemical applications.

Table S2: TD-DFT calculated lowest excited singlet states and character of the transitions for the PV1 monomer ([PV]<sub>1</sub>), dimer ([PV]<sub>2</sub>) and trimer ([PV]<sub>3</sub>).  $\lambda_{cal}$  is the calculated  $\lambda_{max}$  and f is the oscillator strength.

[PV1]	Electronic transition assignment (%)	$\lambda_{cal}$ (nm)	f
	HOMO $\rightarrow$ LUMO (70%)	437.89	0.005
<b>FDX/1</b> 1	HOMO-2   HOMO-1 $\rightarrow$ LUMO (35%   61%)	376.01	0.13
[ <b>P V I J</b> <sub>1</sub>	HOMO-2   HOMO-1 $\rightarrow$ LUMO (60%   36%)	364.09	0.19
	HOMO-6   HOMO-7 $\rightarrow$ LUMO (41%   54%)	251.56	0.81
	HOMO $\rightarrow$ LUMO (70%)	447.63	0.005
	HOMO-2   HOMO-1 $\rightarrow$ LUMO (44%   53%)	384.57	0.41
$[PV1]_2$	HOMO-2   HOMO-1 $\rightarrow$ LUMO (52%   44%)	374.51	0.46
	HOMO-3 $\rightarrow$ LUMO+1 (62%)	365.98	0.23
	HOMO-13 $\rightarrow$ LUMO+1 (66%)	252.05	0.83
	HOMO $\rightarrow$ LUMO (70%)	419.27	0.00
	HOMO-2   HOMO-1 $\rightarrow$ LUMO+1 (47%   50%)	385.91	0.63
	HOMO-3 $\rightarrow$ LUMO (62%)	379.35	0.86
	Homo-2   Homo-1 $\rightarrow$ Lumo+1 (50%   44%)	374.10	0.12
<b>[PV1]</b> <sub>3</sub>	HOMO-6 $\rightarrow$ LUMO (44%)	365.13	0.13
	HOMO-4 $\rightarrow$ LUMO+2 (40%)	365.13	0.13
	HOMO-6 $\rightarrow$ LUMO (41%)	363.37	0.12
	HOMO-4 $\rightarrow$ LUMO+2 (44%)	363.37	0.12
	HOMO-20 $\rightarrow$ LUMO+1 (64%)	251.33	0.98

Table S3: TD-DFT calculated lowest excited singlet states and character of the transitions for the  $PVN_U$  monomer ([PV]<sub>1</sub>), dimer ([PV]<sub>2</sub>) and trimer ([PV]<sub>3</sub>).  $\lambda_{cal}$  is the calculated  $\lambda_{max}$  and f is the oscillator strength.

$\mathbf{PVN}_U$	Electronic transition assignment (%)	$\lambda_{cal}$ (nm)	f
	HOMO $\rightarrow$ LUMO (70%)	488.70	0.02
	HOMO-1 $\rightarrow$ LUMO (70%)	444.51	0.13
$[\mathbf{PVN}_U]_1$	HOMO-4 $\rightarrow$ LUMO (67%)	335.89	0.11
	HOMO-7   HOMO-9 $\rightarrow$ LUMO (45%   30%)	253.00	0.76
	HOMO $\rightarrow$ LUMO+5 (30%)	253.00	0.76
	HOMO $\rightarrow$ LUMO (70%)	540.12	0.03
	HOMO-1   HOMO-2 $\rightarrow$ LUMO (68%   15%)	495.96	0.15
	HOMO-1   HOMO-2 $\rightarrow$ LUMO (16%   68%)	479.86	0.12
$[\mathbf{PVN}_U]_2$	HOMO-1 $\rightarrow$ LUMO+1 (66%)	450.77	0.16
	HOMO-7 $\rightarrow$ LUMO (67%)	362.09	0.24
	HOMO-7   HOMO-8   HOMO-9 $\rightarrow$ LUMO (17%   45%   45%)	333.56	0.15
	$HOMO-25 \rightarrow LUMO~(47\%)$	254.94	0.47
	HOMO $\rightarrow$ LUMO (70%)	539.30	0.00
	HOMO-1 $\rightarrow$ LUMO+1 (67%)	479.80	0.23
$[\mathbf{PVN}_U]_3$	HOMO-4 $\rightarrow$ LUMO (64%)	457.61	0.14
	HOMO-3 $\rightarrow$ LUMO+1 (62%)	452.10	0.23
	HOMO-22 $\rightarrow$ LUMO+1 (30%)	258.00	0.22

Table S4: TD-DFT calculated lowest excited singlet states and character of the transitions for the  $PVN_V$  monomer ([PV]<sub>1</sub>), dimer ([PV]<sub>2</sub>) and trimer ([PV]<sub>3</sub>).  $\lambda_{cal}$  is the calculated  $\lambda_{max}$  and f is the oscillator strength.

$\mathbf{PVN}_V$	Electronic transition assignment (%)	$\lambda_{cal}$ (nm)	f
	HOMO $\rightarrow$ LUMO (67%)	441.40	0.09
$[\mathbf{PVN}_V]_1$	HOMO-2   HOMO-1 $\rightarrow$ LUMO (62%   30%)	404.54	0.20
	HOMO-8 $\rightarrow$ LUMO (58%)	253.82	0.85
	HOMO $\rightarrow$ LUMO (68%)	459.96	0.18
	HOMO-2   HOMO $\rightarrow$ LUMO (67%   14%)	431.79	0.43
$[\mathbf{PVN}_V]_2$	HOMO-3 $\rightarrow$ LUMO+1 (70%)	406.96	0.30
	HOMO-25 $\rightarrow$ LUMO (41%)	253.57	1.16
	HOMO $\rightarrow$ LUMO+10 (42%)	253.57	1.16
	HOMO   HOMO-4 $\rightarrow$ LUMO+1 (67%/15%)	461.33	0.20
	HOMO-2 $\rightarrow$ LUMO (47%)	436.92	0.79
$[\mathbf{PVN}_V]_3$	HOMO-6   HOMO-3   HOMO $\rightarrow$ LUMO (13%   40%   16%)	422.96	0.18
	HOMO-5   HOMO-3   HOMO-2 $\rightarrow$ LUMO+1 (44%   34%   36%)	411.17	0.26
	$HOMO-25 \rightarrow LUMO+1 \ (59\%)$	253.27	1.64

Table S5: Internal reorganization energies in vacuum ( $\lambda_r$ ), free energy change of reduction halfreaction in solution ( $\Delta G_r$ ) and reductive potential ( $E_r$  eq. 6) for PV1.

PV1	$\lambda_r$ (eV)	$\Delta \mathbf{G}_r$ (eV)	$\mathbf{E}_{r}\left(\mathbf{V}\right)$
$\overline{[\text{PV1}]_{1}^{+2} + e^{-} \to [\text{PV1}]_{1}^{+1}}$	0.20	-4.50	-0.16
$[PV1]_1^{+1} + e^- \rightarrow [PV1]_1^0$	0.15	-3.46	-1.20
$\overline{[\text{PV1}]_2^{+4} + e^-} \to [\text{PV1}]_2^{+3}$	0.12	-4.62	-0.05
$[PV1]_2^{+3} + e^- \rightarrow [PV1]_2^{+2}$	0.16	-3.61	-1.05
$[PV1]_2^{+2} + e^- \rightarrow [PV1]_2^{+1}$	0.08	-4.47	-0.19
$[PV1]_2^{+1} + e^- \rightarrow [PV1]_2^0$	0.10	-3.50	-1.16

Table S6: Internal reorganization energies in vacuum ( $\lambda_r$ ), free energy change of reduction halfreaction in solution ( $\Delta G_r$ ) and reductive potential ( $E_r$  eq. 6) for PVN<sub>U</sub>.

<b>PVN</b> <sub>U</sub>	$\lambda_r$ (eV)	$\Delta \mathbf{G}_r$ (eV)	$\mathbf{E}_{r}$ (V)
$[\mathbf{PVN}_U]_1^{+2} + e^- \to [\mathbf{PVN}_U]_1^{+1}$	0.25	-4.35	-0.32
$[\mathbf{PVN}_U]_1^{+1} + e^- \to [\mathbf{PVN}_U]_1^0$	0.26	-3.49	-1.17
$[\mathbf{PVN}_U]_2^{+4} + e^- \to [\mathbf{PVN}_U]_2^{+3}$	0.17	-4.55	-0.11
$[\mathrm{PVN}_U]_2^{+3} + e^- \to [\mathrm{PVN}_U]_2^{+2}$	0.18	-4.36	-0.30
$[\mathrm{PVN}_U]_2^{+2} + e^- \to [\mathrm{PVN}_U]_2^{+1}$	0.20	-3.94	-0.71
$[\mathbf{PVN}_U]_2^{+1} + e^- \to [\mathbf{PVN}_U]_2^0$	0.25	-3.42	-1.24

$\mathbf{PVN}_V$	$\lambda_r$ (eV)	$\Delta \mathbf{G}_r$ (eV)	$\mathbf{E}_{r}\left(\mathbf{V}\right)$
$\overline{[\mathbf{PVN}_V]_1^{+2} + e^-} \to [\mathbf{PVN}_V]_1^{+1}$	0.19	-4.39	-0.28
$[\mathbf{PVN}_V]_1^{+1} + e^- \to [\mathbf{PVN}_V]_1^0$	0.24	-3.48	-1.19
$\overline{[\mathbf{PVN}_V]_2^{+4} + e^-} \to [\mathbf{PVN}_V]_2^{+3}$	0.11	-4.47	-0.19
$[\mathrm{PVN}_V]_2^{+3} + e^- \to [\mathrm{PVN}_V]_2^{+2}$	0.10	-3.74	-0.92
$[\mathrm{PVN}_V]_2^{+2} + e^- \to [\mathrm{PVN}_V]_2^{+1}$	0.09	-4.35	-0.31
$[\mathrm{PVN}_V]_2^{+1} + e^- \to [\mathrm{PVN}_V]_2^0$	0.14	-3.50	-1.17

Table S7: Internal reorganization energies in vacuum ( $\lambda_r$ ), free energy change of reduction halfreaction in solution ( $\Delta G_r$ ) and reductive potential ( $E_r$  eq. 6) for PVN<sub>V</sub>.

# S7 FTIR-ATR spectroscopy



Figure S28: FTIR-ATR spectra of the studied polyviologens

## **S8** Performance Measurements

This section presents the performance metrics of our photocapacitors under various lighting conditions. We include J-V characteristics, photocharge measurements, and comparisons between different device configurations to demonstrate the efficiency and versatility of our photocapacitors.



Figure S29: J-V measurements of the PV component of 24 photocapacitors with a mask of 0.16  $\text{cm}^2$  and full active area 0.28  $\text{cm}^2$  under AM 1.5G illumination, at a) 1 sun and b) 0.1 sun.



Figure S30: Statistics for the J-V measurements of 24 photocapacitors under AM 1.5G illumination, at 1 sun and 0.1 sun, with a mask of 0.16 cm<sup>2</sup> and full active area 0.28 cm<sup>2</sup>



Figure S31: Photocharge measurements of photocapacitors PV1//CH//C under (left) 1 sun and (right) 0.1 sun illumination, and self-discharge under dark conditions



Figure S32: Photocharge measurements of photocapacitors PV1//N//C under (left) 1 sun and (right) 0.1 sun illumination, and self-discharge under dark conditions



Figure S33: Photocharge measurements of photocapacitors PVN//CH//C under (left) 1 sun and (right) 0.1 sun illumination, and self-discharge under dark conditions



Figure S34: Photocharge measurements of photocapacitors PVN//N//C under (left) 1 sun and (right) 0.1 sun illumination, and self-discharge under dark conditions



Figure S35: Photocapacitors of 4.2 cm<sup>2</sup> photoactive area and 1.5 cm<sup>2</sup> supercapacitor electrodes



Figure S36: Light spectra and integrated irradiance at 1000 lx for the light sources in the ambient set-up, a) Cold LED 4000 K and b) Osram CFL4000K



Figure S37: J-V measurements of the PV component (DSC) of 16 photocapacitors under 1000 lx from an , with a mask of 3.38 cm<sup>2</sup> and full active area 4.2 cm<sup>2</sup>. For all the measurements the solid line refers to measurements with no mask, while the dash lines represent masked devices. The measurements were performed under a) and b) an OSRAM CFL light and c) and d) under a Cold LED 4000 K.



Figure S38: Statistics for the J-V measurements of 16 photocapacitors under 1000 lx from an OSRAM CFL light at forward bias (FB) and reverse bias (RB), with a mask of 3.38 cm<sup>2</sup> and full active area 4.2 cm<sup>2</sup>.



Figure S39: Statistics for the J-V measurements of 16 photocapacitors under 1000 lx from an LED lamp, with a mask of  $3.38 \text{ cm}^2$  and full active area  $4.2 \text{ cm}^2$ 



Figure S40: Photocharge measurements, CFL light on during 3 mins and light off, discharge current 1  $\mu$ A



Figure S41: Photocapacitors connected in series connected to IoTs to power machine learning, total area 25.2 cm<sup>2</sup> reaching 5.31 V under fluorescent lighting conditions in the laboratory bench



Figure S42: Indoor set-up calibration with spectroradiometer

# **S9** IoT, Edge Computing

In this final section, we showcase the application of our photocapacitors in IoT networks and edge computing scenarios. We present network topologies, device benchmarks, and MNIST prediction tests to illustrate the potential of our devices in powering continuous edge computing in ambient-powered IoT networks.



(a) 1-layer star IoT network topology

(b) 3-layer tree IoT network topology

Figure S43: Benchmarked IoT network topologies.



(c) D2 - Device 2 - Photocapacitor

Figure S44: Photocapacitor 24 hour individual IoT device benchmark in single-layer deployment at 1000 lx for devices D2, D1, and D3 with average sleep times of 342.1 ms, 268.5 ms, and 277.8 ms respectively.



(c) D0 - Device 0 - Powerfilm

Figure S45: Powerfilm 24 hour individual IoT device benchmark in single-layer deployment at 1000 lx for devices D0, D4, and D5 with average sleep times of 650.9 ms, 700.3 ms, and 586.4 ms respectively.



Figure S46: 72 hour MNIST prediction L3-test at 1000 lx, resulting in 1.90 MNIST predictions per hour for the photocapacitor network, and 0.54 predictions per hour for the powerfilm network.



(c) Channel 1 - Layer 3 - Photocapacitor

Figure S47: 72 hour MNIST prediction L3-test at 250 lx, resulting in 0.10 MNIST predictions per hour for the photocapacitor network, and 0.03 predictions per hour for the powerfilm network.

## References

- Beladi-Mousavi, S. M., Sadaf, S., Mahmood, A. M. & Walder, L. High Performance Poly(viologen)–Graphene Nanocomposite Battery Materials with Puff Paste Architecture. *ACS Nano* 11, 8730–8740 (2017).
- Pérez-Bassart, Z., Fabra, M. J., Martínez-Abad, A. & López-Rubio, A. Compositional differences of β-glucan-rich extracts from three relevant mushrooms obtained through a sequential extraction protocol. *Food Chemistry* **402**, 134207 (2023).
- 3. Pérez-Bassart, Z. *et al.* Antiviral and technological properties of  $\beta$ -glucan-rich aqueous fractions from *Pleurotus ostreatus* waste biomass. *Food Hydrocolloids* **146**, 109308 (2024).
- 4. Michaels, H. *et al.* Emerging indoor photovoltaics for self-powered and self-aware IoT towards sustainable energy management. *Chem. Sci.* **14**, 5350–5360 (2023).
- 5. Frisch, M. J. et al. Gaussian 16 (2016).
- 6. Adamo, C. & Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *The Journal of Chemical Physics* **110**, 6158–6170 (1999).
- Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *The Journal of Chemical Physics* 132, 154104 (2010).
- Tomasi, J., Mennucci, B. & Cammi, R. Quantum Mechanical Continuum Solvation Models. *Chem. Rev.* 105, 2999–3094 (2005).
- Patankar, S. C. & Yadav, G. D. Cascade engineered synthesis of 2-ethyl-1-hexanol from *n*-butanal and 2-methyl-1-pentanol from *n*-propanal using combustion synthesized Cu/Mg/Al mixed metal oxide trifunctional catalyst. *Catalysis Today* 291, 223–233 (2017).
- Busch, M., Laasonen, K. & Ahlberg, E. Method for the accurate prediction of electron transfer potentials using an effective absolute potential. *Phys. Chem. Chem. Phys.* 22, 25833–25840 (2020).