Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Non-contact Computer Vision Enables Analysis of the Dynamic Performance of Naphthalene Diimide Electrochromic Films

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SUPPORTING INFORMATION

1. Synthetic Procedures and Characterisation

The chemicals and solvents used were all purchased from Sigma-Aldrich, Alfa Aesar, and Hyaltech Ltd. Naphthalenetetracarboxylic dianhydride (NTCDA) was found *via* spectroscopic measurements to have been impure upon purchasing. The procedure used to purify the NTCDA has previously been described by our group.[1] Hyaluronic acid (HA) was dried *via* lyophilisation prior to use. All other chemicals were used as received. Deionised water was used throughout.

To the best of our knowledge, **NDI-L** and **NDI-M** (1.1 and 1.2) have not been previously reported. The synthetic route reported here used to synthesise **NDI-L** and **NDI-M** was adapted from a method previously described by our group.[1] Full synthetic procedures and characterisation of **PBI-L** has previously been reported.[2]

When synthesising and storing the NDI, it is important that it is not exposed to UV light. UV light is known to reduce the NDI to the radical anion. This results in the compound taking on a dark brown colour, which is difficult to remove from the solid material. To prevent this, the reaction is covered in aluminium foil and the light of the fume hood was turned off. The resulting product was also covered with foil and stored inside of a cupboard until use. The purified NTCDA was stored in amber glass.

1.1 Synthesis of (2S)-2-{13-[(1S)-1-carboxy-3-methylbutyl]-5,7,12,14-tetraoxo-6,13-diazatetracyclo[6.6.2.04,16011,15]hexadeca-1,3,8(16),9,11(15)-pentaen-6 yl} -4-methylpentanoicacid (NDI-L)

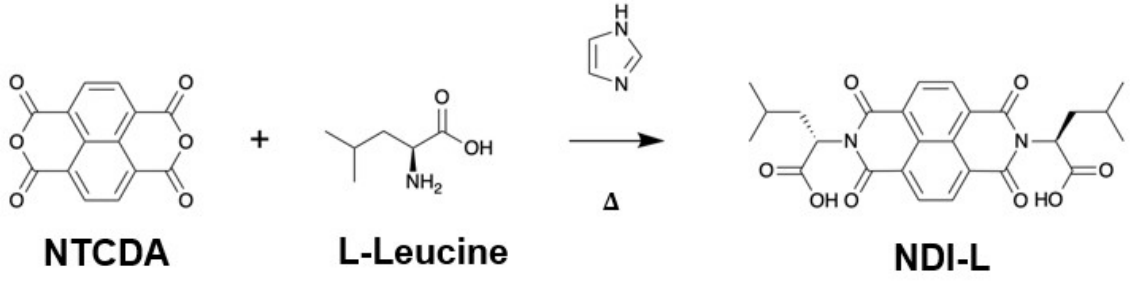


Figure S1: *Synthesis of* ***NDI-L***

Napthalene-1,4,5,8-tetracarboxylic acid dianhydride (NTCDA, 2.00 g, 7.46 mmol), L-leucine (2 eq, 1.96 g, 14.9 mmol) and imidazole (10 eq, 5.08 g, 74.6 mmol) were added to a Schlenk flask and degassed with nitrogen for 5 minutes. The solids were then heated to 120°C and stirred under nitrogen for 5 hours. This was performed in the dark to prevent the formation of the reduced species. The temperature was then lowered to 90 °C and 50 mL of water was added, and then the mixture was stirred for 1 hour. The mixture was then filtered, and the filtrate was poured into 200 mL of 2M HCl (aq) and stirred for 30 minutes. The mixture was filtered, and the precipitate was washed with water until the pH was no longer acidic. Crude NMR indicated the presence of impurities. The crude solid was then then added to 200 mL of 1M HCl (aq) and stirred at 90 °C for 1 hour. The mixture was then filtered, and the precipitate was washed with water until the pH was no longer acidic. The solid was frozen and lyophilised overnight to yield a light grey solid (2.86 g, 77.2%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.92 (br s, 1H, COO<u>H</u>), 8.74 (s, 4H, naphthalene core), 5.58 (dd, J = 8.9 Hz, 5.0 Hz, 2 H, NC<u>H</u>$_2$) 2.14-1.96 (m, 4H, C<u>H</u>$_2$) 1.62-1.51 (m, 2H, C<u>H</u>), 0.94 (d, J = 6.5, 6H, C<u>H</u>$_3$), 0.86 (d, J = 6.5, C<u>H</u>$_3$). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.9 (COOH), 162.4 (C=O), 131.2, 126.3, 126.0 (naphthalene core), 51.8 (NCH), 37.6 (CH_2), 24.8 ($CH(CH_3)$), 22.9 (CH_3), 21.9 (CH_3). HRMS (ESI) m/z: $[M+H]^+$ calculated for $C_{26}H_{27}N_2O_8$, 495.1689; found 495.17.

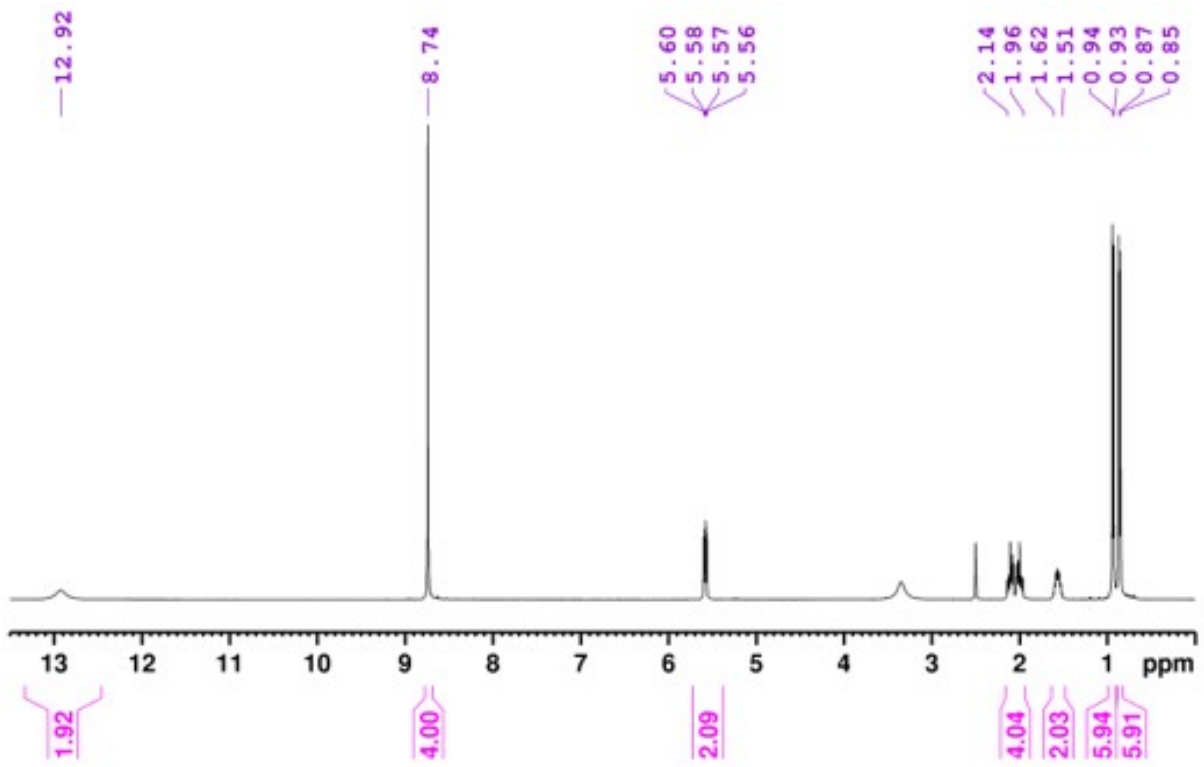


Figure S2: *^{1}H NMR spectrum (400 MHz, DMSO-d_6) of* ***NDI-L***

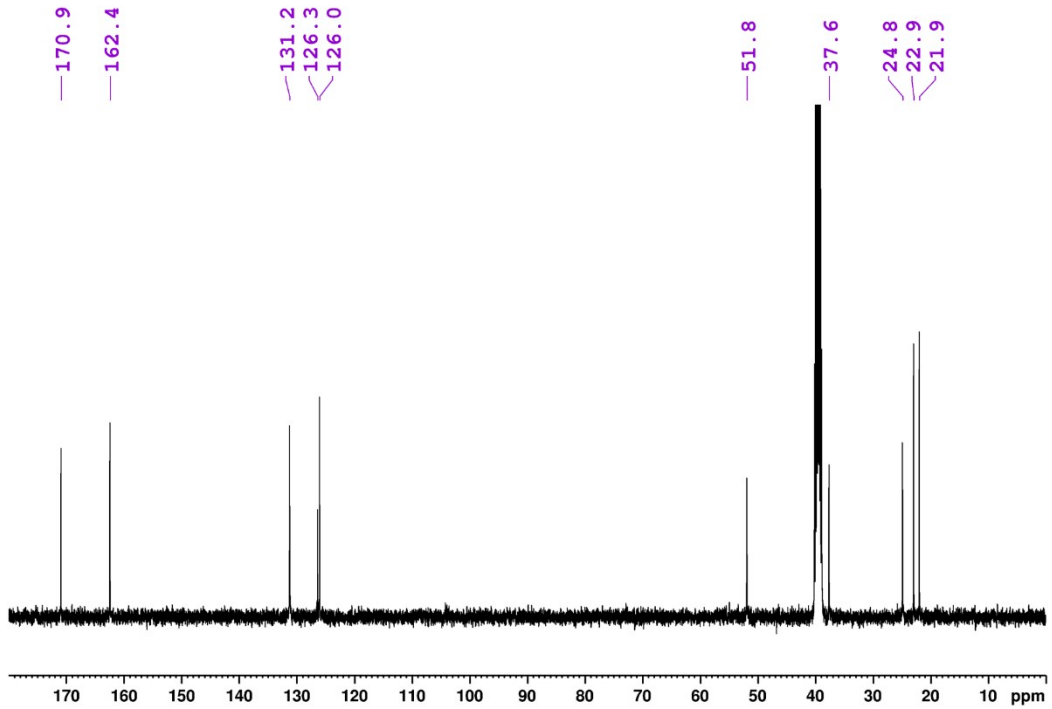


Figure S3: *^{13}C NMR spectrum (100 MHz, DMSO-d_6) of* ***NDI-L****.*

1.2 Synthesis of (2S)-2-{13-[(1S)-1-carboxy-3-(methylsulfanyl)propyl]-5,7,12,14-tetraoxo-6,13-diazatetracyclo [6.6.2.0^{4,16}0^{11,15}]hexadeca-1,3,8(16),9,11(15)-pentaen-6-yl}-4-(methylsulfanyl)butanoicacid (NDI-M)

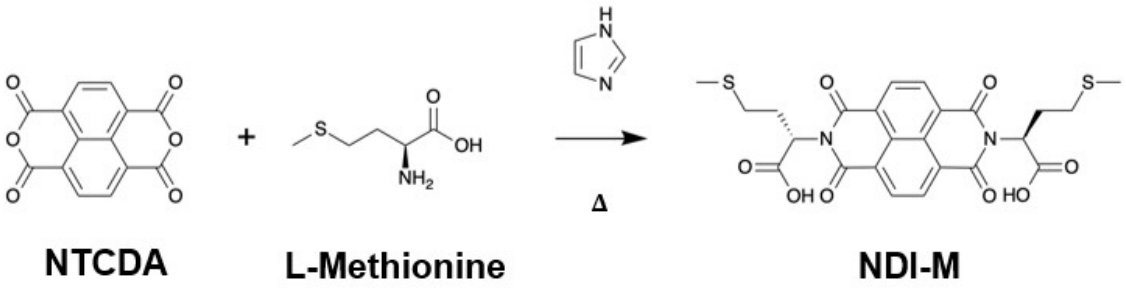


Figure S4: *Synthesis of* ***NDI-M***

The reaction was performed following the procedure outlined above (section 1.1) using the amino acid L-Methionine (2 eq, 2.23 g, 14.9 mmol). The final product was isolated as a yellow solid (2.25 g, 57.0%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.97 (br s, 2H, COOH), 8.74 (s, 4H, naphthalene core), 5.73-5.69 (m, 2 H, NCH) 2.61-2.54 (m, 6H, CH_2) 2.34-2.23 (m, 2H, CH_2), 2.00 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.0 (COOH), 163.0 (C=O), 131.5, 126.9, 126.7 (naphthalene core), 53.0 (NCH), 30.9 (CH_2), 28.4 (SCH_2), 14.9 (SCH_3). HRMS (ESI) m/z: $[M+Na]^+$ calculated for $C_{26}H_{22}N_2O_8S_2Na$, 553.0715; found 553.0709.

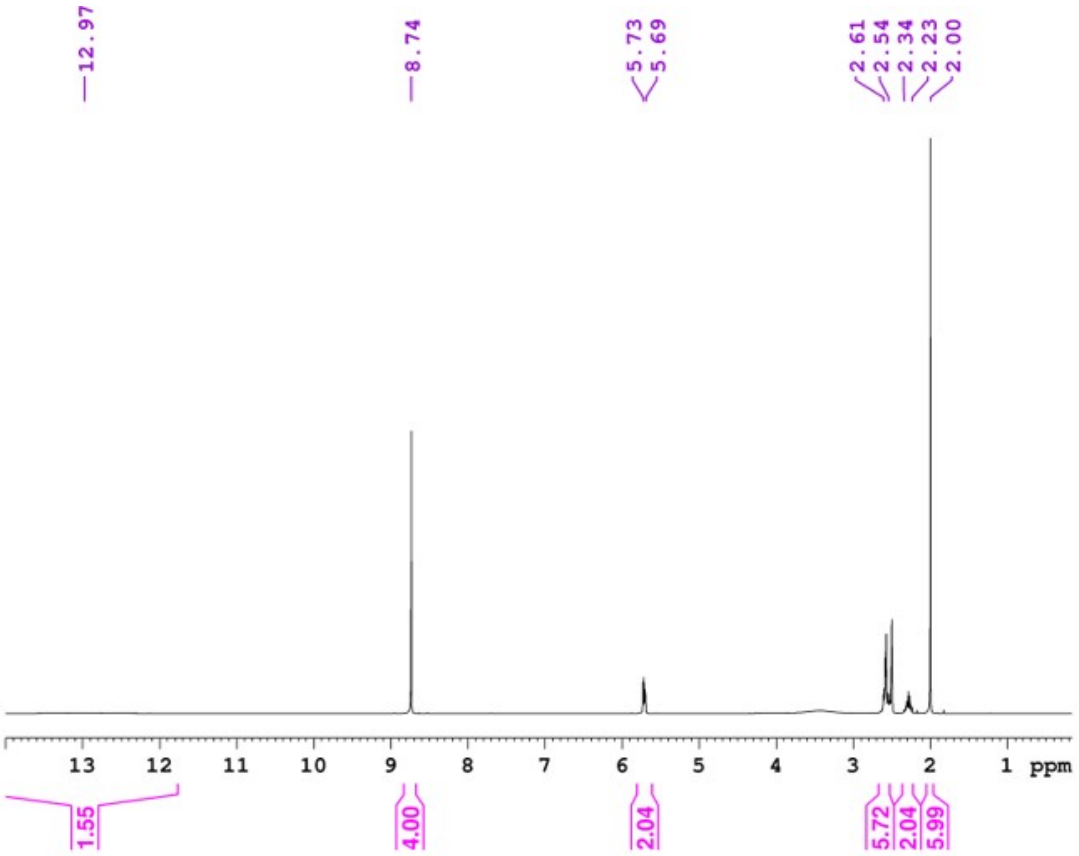


Figure S5: *^{1}H NMR spectrum (400 MHz, DMSO-d_6) of* ***NDI-M***

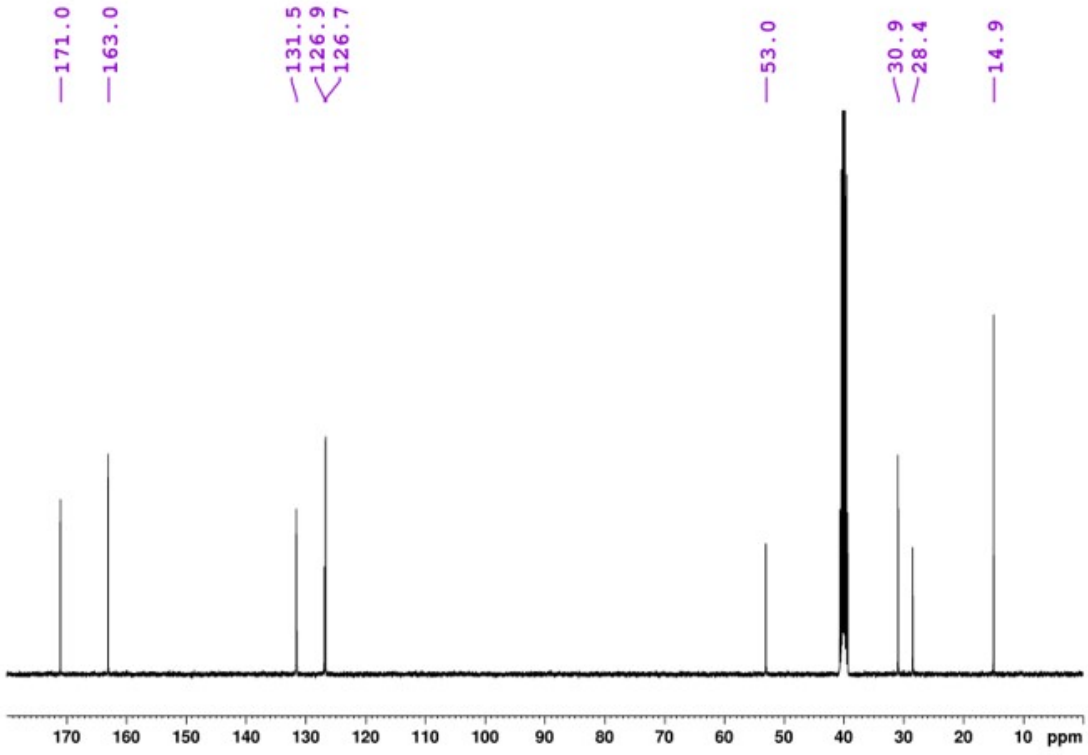


Figure S6: ^{13}C NMR spectrum (100 MHz, DMSO-d6) of **NDI-M**

2. Experimental Protocols and Equipment

2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Carbon and proton NMR spectroscopy measurements were collected using a Bruker 400 MHz spectrometer. All samples were ran using deuterated dimethyl sulfoxide (DMSO) as the solvent. The spectrometer operated at 400 MHz for ^{1}H NMR and 101 MHz for ^{13}C NMR spectroscopy.

2.2 High Resolution Mass Spectroscopy (HRMS)

HRMS measurements were carried out using a Bruker microTOFq Mass Spectrometer. Electrospray ionisation was used and was coupled to a time-of-flight analyser. The instrument is accurate to <5 ppm. Samples were run in ethanol. Measurements were carried out by the University of Glasgow mass spectrometry service.

2.3 Lyophilisation

Synthetic products were dried using lyophilisation. Solids were first neutralised by washing with large amounts of water, which was performed until the washings were no longer acidic. This was tested using universal indicator paper purchased from Merch Life Sciences. Solids were then frozen in a freezer set to -18 ºC. Water was then removed using a LSCBasic Freeze-dryer at -85 ºC and between 0.890 and 1.25 mBar.

2.4 pH Measurements

The pH of solutions was measured using an FC200 pH prove (HANNA Instruments) with a 6 mm x 10 mm conical tip calibrated using buffers of pH 4, 7 and 10 (HANNA Instruments). The stated accuracy of the pH probe is ±0.1.

2.5 Spectro-Electrochemistry (SEC)

Solutions for spectro-electrochemistry (SEC) were prepared at a concentration of 0.5 mg/mL and were dispersed in 2 molar equivalents of NaOH (1M, aq). NaCl (0.1 M, aq) was added at a concentration of 0.4 mL/mL of total solution. The remaining volume of solution was made up using deionised water. The solutions were adjusted to a pH of 6 or 9 with HCl (1 M, aq) and NaOH (1 M, aq) using a HANNA instruments pH probe.

SEC was performed in an EF-1350 SEC-C thin layer quartz glass SEC cell (BASi) with a platinum gauze working electrode, a platinum counter electrode, and an aqueous reference electrode (Ag/AgCl). CV measurements were first performed in the SEC cell, using a voltage range of -0.8 V to -0.2 V. An equilibration time of 5 second was used. Scan rates of 500, 100, and 50 mV/s were utilised and a total of 5 scans were collected for each measurement. The solutions were degassed with nitrogen gas prior to the start of experimentation.

The absorbance of the solution was measured *in-situ* using a Cary 60 UV-vis spectrophotometer from Agilent Technologies. A baseline measurement was collected in water. Spectra were collected from 200 nm to 1000 nm at a scan rate of 4800 nm/min. Measurements were collected by the spectrometer every 2 minutes. Using the voltages identified from CV measurements, the solution was electrochemically reduced for a total of 20 minutes unless otherwise stated. The solution was then oxidised until the absorbance was seen to plateau. The solution was allowed to oxidise in air for an additional 10 minutes before a final measurement was taken.

2.6 Solutions for Film Formation

To prepare films, solutions were prepared with an NDI concentration of 5 mg/mL and were dispersed in 2 molar equivalents of NaOH (1M, aq) and the necessary volume of deionised water. The resulting solutions were stirred overnight. HA was added to the solutions at a concentration of 15 mg/mL and stirred for an additional 72 hours. This resulted in the formation of a viscous solution which, upon drying, created suitably uniform and durable films. The solutions were adjusted to their ideal pH with HCl (1 M, aq) and NaOH (1 M, aq) using a HANNA instruments pH probe. The solutions were then suitable for film processing. All NDI/HA solutions were used within one week of

preparation. PBI solutions were prepared at 5 mg/mL and were dispersed in 1 molar equivalent of NaOH (0.1 M, aq) and necessary volume of deionised water. The resulting solutions were stirred overnight. The pH was raised to 7.5 using NaOH (1M, aq) to ensure PBI was fully dispersed. HA was added to the solutions at a concentration of 15 mg/mL and stirred for an additional 72 hours.

2.7 FTO Glass

FTO glass (Ossilia S2002S1, NSG TEC 10) with the dimensions of 20 mm by 15 mm and a thickness of 1 mm was used. The FTO has a quoted resistance of 11-13 Ω/sq. A small piece of copper tape was added to one edge of the glass to allow the passage of current into the glass. The glass was plasma treated for 20 minutes using a Plasma Cleaner Zepto M2 from Diener Electronics. The FTO glass was plasma cleaned with oxygen plasma prior to film casting. Plasma cleaning is a process by which oxygen plasma is used to remove organic contaminants from the surface of the material, while also introducing functional groups onto the surface. This results in a more hydrophilic surface on which the films can adhere to. The glass was used immediately after plasma cleaning.

2.8 Thin Film Formation

The films were prepared on FTO glass using the Doctor Blade. The NDI/HA solution was added to the top edge of the glass using a pipette. The Doctor Blade was set to a height of 3.5 mm. As the glass itself had a height of 2 mm, this resulted in the formation of films with a thickness of 1.5 mm. The Doctor Blade was moved parallel across the glass surface, thereby depositing the solution across the length of the glass. A casting speed of 10 mm/s and casting distance of 40 mm were used. The glass was then heated to 80 °C for 1 hour, causing the water in the solvent to evaporate and the film to dry down and adhere to the glass surface. This process is represented graphically in Figure S7.This resulted in the formation of the NDI/HA film which showed, using optical microscopy, no obvious structural defects and were therefore suitable for further experimentation (Section 3.3). The **PBI-L** films were cast at a thinner thickness of 0.5 mm. This was to ensure the film was not so strongly coloured that any electrochromic response could not be seen.

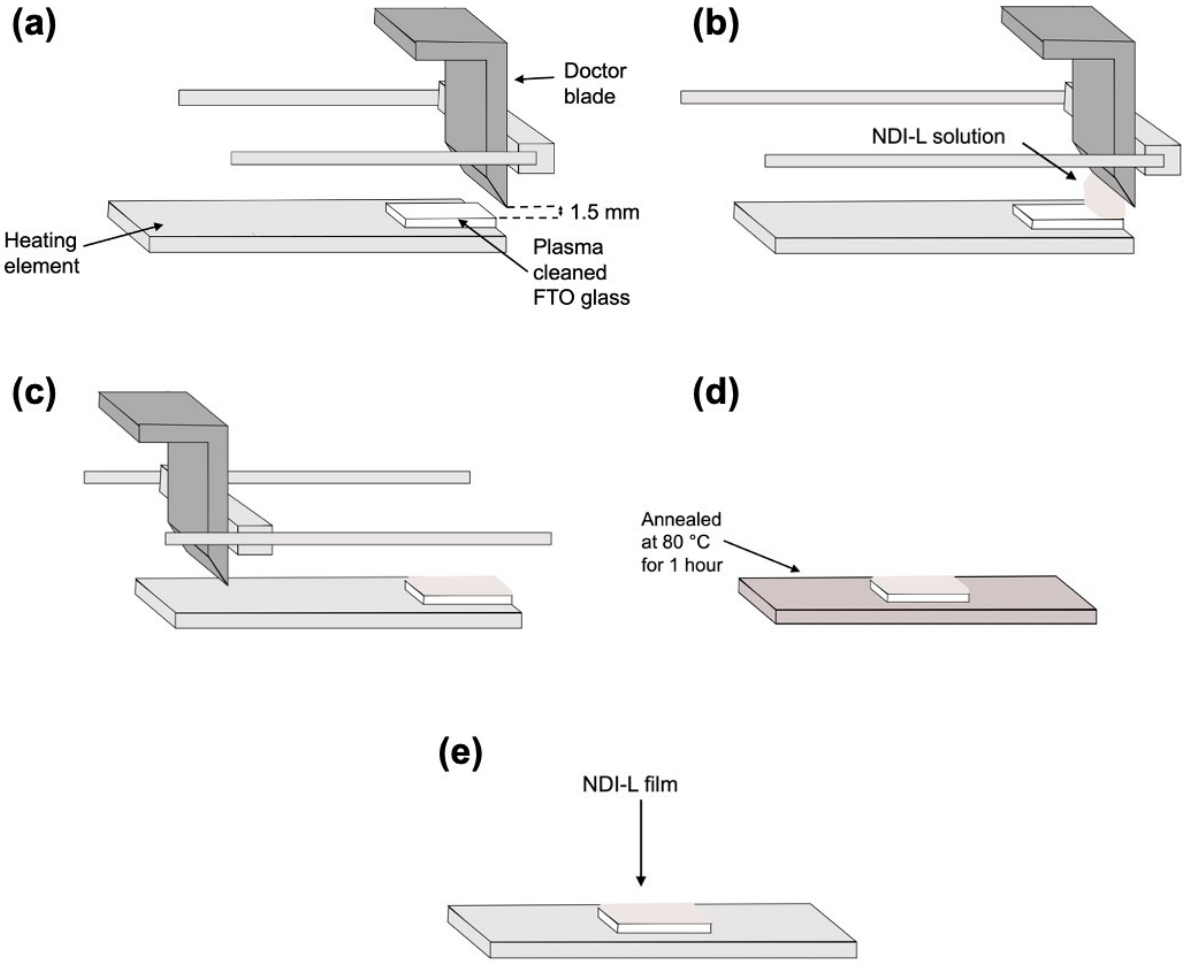


Figure S7: *Overview of thin film casting on FTO glass using doctor blade, showing* ***(a)*** *calibration and set-up of the doctor blade,* ***(b)*** *addition of NDI solution, (****c****) casting of solution across glass surface, (****d****) thermal annealing of solution to glass, and* ***(e)*** *the completed NDI film.*

2.9 Optical Microscopy

Images were collected using a Nikon Eclipse LV100 microscope with a Nikon Plan ELWD x5 lens attached to an Infiinity2-1C camera. No post modification or processing were made to the images after being collected.

2.10 Electrochemistry Setup

Electrochemistry was performed using a PalmSens4 potentiostat. A three-electrode setup was utilised for both solution and film-based electrochemistry. To test the films, an electrolytic solution of dichloromethane (DCM) and 0.1 M tetrabutylammonium

hexafluorophosphate (TBAHFP) was prepared and degassed with nitrogen gas for 10 minutes. The FTO glass, functioning as a working electrode, was suspended in the solution, in addition to a platinum wire counter electrode and an organic reference electrode containing 0.01 M $AgNO_3$ in acetonitrile. A diagram of the electrochemical set-up is shown in Figure S8.

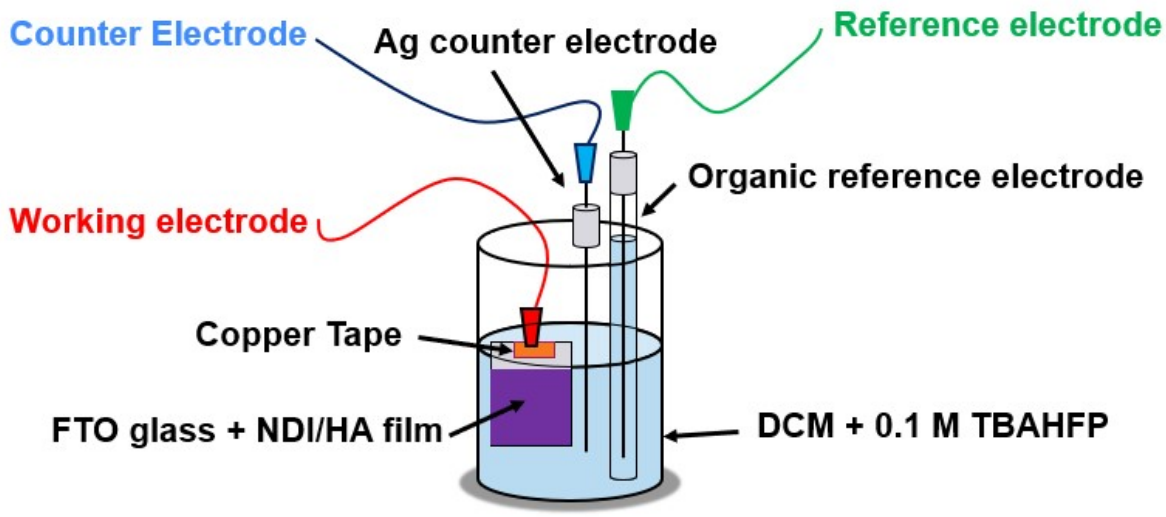


Figure S8: *Schematic of electrochemistry set-up.*

2.11 Cyclic Voltammetry (CV)

CV measurements of films were performed in the electrochemical setup described above (Section 2.10). A voltage range of -2.0 V to 2.0 V was tested. The electrolytic DCM/TBAHFP solution was degassed with nitrogen gas prior to experimentation. A scan rate of 200, 100 and 50 mV/s were utilised and a total of 5 scans were collected for each measurement. An equilibration time of 5 seconds was applied.

2.12 Electrochromic Behaviour of Films

Electrochemistry was performed on the films using the previously described electrochemistry set-up (Section 2.10) and the response measured using absorption spectroscopy or *Kineticolour*. The NDI films were reduced *via* application of -1.8 V. To oxidise the films, after electrochemical reduction, a potential of +2.0 V was applied. These potentials were chosen from CV measurements (Section 3.4). Cyclability

measurements were performed by electrochemically reducing and oxidising the film over 10 cycles. The PBI films were reduced using a potential of -1.2 V. A lower potential was used to minimise the amount of PBI being electrochemically stripped from the film and leeching into the bulk electrolyte, which in turn could interfere with the Kineticolor outputs.

2.13 UV-Vis Absorption Spectroscopy

All UV-vis absorption spectroscopy measurements were collected using a Cary 60 UV-vis spectrophotometer from Agilent Technologies. Spectra were collected from 300 nm to 1000 nm. A scan rate of 600 nm/min was used. Film measurements were performed on solid NDI/HA thin films on fluorine doped tin oxide (FTO) glass, and baseline measurements were performed on clean FTO glass. A 3D printed holder was used to hold the films inside the spectrometer during measurements, which ensured the same area was measured throughout the duration of the experiment. Transmission measurements were collected in the same set-up. Colouration homogeneity was investigated by measuring the absorbance at 9 different areas of the film following electrochemical reduction.

2.14 Colouration Efficiency

Coloration efficiencies of our films were calculated using the following equation:[3]

$$CE = \frac{\log\left(\frac{T_b}{T_C}\right)_\lambda}{Q_d} \qquad \text{(Equation 1)}$$

Where T_b and T_c is the transmission of the film in the bleached and coloured state, respectively. T_b and T_c values are measured at the wavelength producing the maximum optical density change. Q_d is the charge density and is calculated by dividing the charge generated by the geometric electrode area of the device.

2.15 Camera Recording Set-Up

The electrochromic response of the film was monitored *in-situ* using a Panasonic HC-W580, filming at a resolution of 780p and a frame rate of 25 fps. All videos were filmed

with manual focus and no auto white balance. This avoided any undue changes in focus or video quality for the duration of each experiment. Unless otherwise stated, all electrochemical measurements were performed in a light box to minimise the effects of ambient light. The camera was also placed inside the lightbox, thereby allowing filming to be undertaken within a completely enclosed lightbox. The two LED light panels were kept on at full power for the duration of each experiment. The resulting video outputs were uploaded to and processed using the *Kineticolor* software package (version 0.3.2).

All videos were analysed by breaking videos into their constituent frames, and each frame being analysed, at the pixel level, in turn. A user-selected region of interest was analysed, averaging all pixel values in the selected range. For the NDI films, all background data outside the selected region was ignored in the analysis. As the PBI films leach into the bulk electrolyte, background measurements of the DCM were also performed. Output machine-readable data related to all figures in the manuscript are available as a separate zipped folder as part of the supporting information. The analysed frames were curated in plots of various colour or mixing components versus time to enable semi-quantitative and comparative kinetic analysis between different video analysis datasets. Extracted colour data were provided from across a common subset of colour models, namely: RGB, HSV, CIE-L*a*b*, and CIE-XYZ. For contact measurements the same greyscale threshold value and same size region of interest was used. A zip folder is provided with submission containing machine-readable Kineticolour outputs for our experiments.

To access a Kineticolor license, contact marc.reid.100@strath.ac.uk and iprmanager@strath.ac.uk.

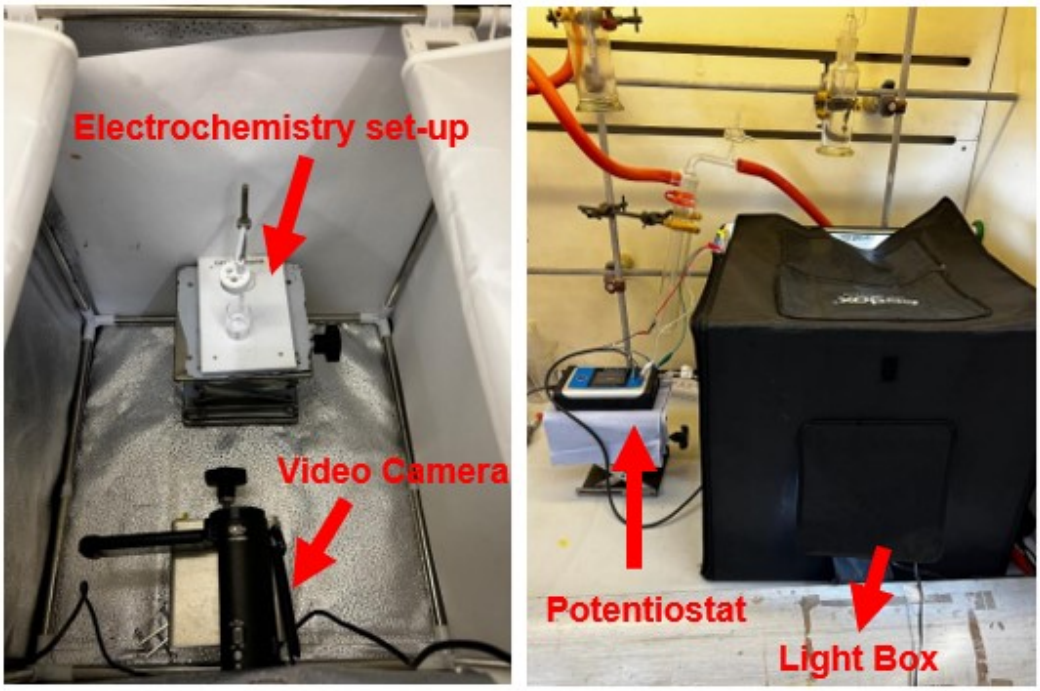


Figure S9: Annotated camera set-up within lightbox (left) and full experimental set-up (right) as it appeared during experiments.

2.16 Photochromic Response

The photochromic response of the film to light irradiation within the lightbox was measured by suspending the film in the box using crocodile clips and monitoring the colour change over time using the previously described camera set-up (Section 2.15) The resulting video outputs were uploaded to and processed using the *Kineticolor* software package.

2.17 Open Bench Response

The electrochromic response of the film in uncontrolled lighting was investigated by electrochemically reducing the film (Section 2.12) outside of the lightbox. The response was monitored using a video camera, and the resulting video outputs were uploaded to and processed using the *Kineticolor* software package. These were run at 55° 51' 46.908" N 4° 14' 34.8" W (Glasgow) on the 25th June 2024 between 11.01 am and 11.21 am. The flux reading in the fume hood at that time was 328 lux, typical of office level lighting.

3. Supplementary Figures

3.1 Colouration Efficiency

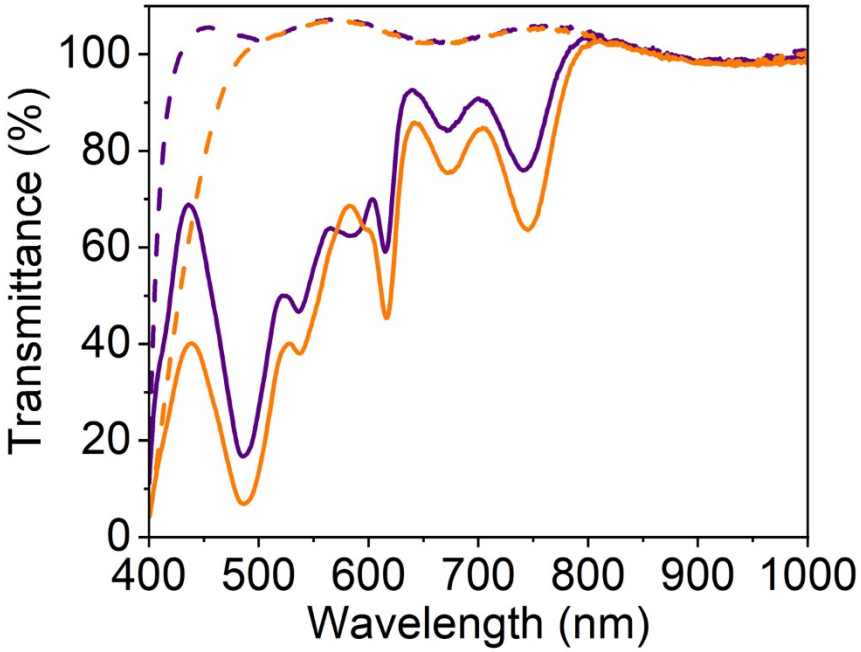


Figure S10: *Transmittance of* ***NDI-L*** *film (purple line) and* ***NDI-M*** *film (orange line) prior to (dashed line) and following (solid line) application of -1.8 V for 20 minutes.*

Table S1: *Tabulated CE calculated from transmittance of* ***NDI-L*** *film and* ***NDI-M*** *film prior to and following application of -1.8 V for 20 minutes. CE calculated using charge density over a 1.5 cm x 1.5 cm electrode surface.*

	% transmittance at 487 nm	Charge (C)	Qd (C/cm^2)	CE (cm^2/C)
NDI-L (neutral state)	103.7	0.05	0.02	39.5
NDI-L (coloured state)	16.8			
NDI-M (neutral state)	100.3	0.10	0.04	29.1
NDI-M (coloured state)	6.9			

3.2 Spectro-Electrochemistry Measurements

3.2.1 CV Measurements

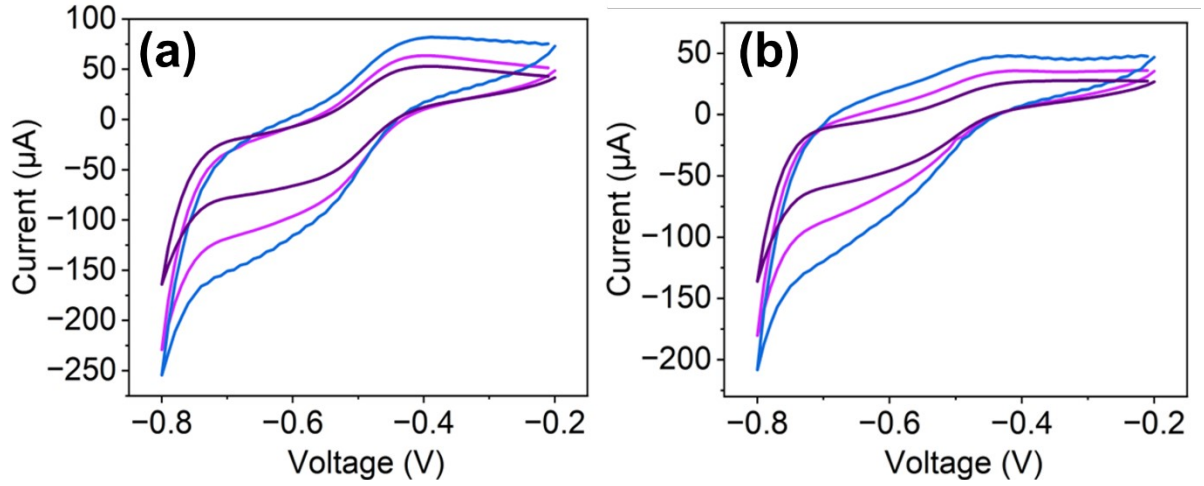


*Figure S11: CV measurement of 0.5 mg/mL **NDI-L** solution at **(a)** pH 6 and **(b)** pH 9 (vs Ag/AgCl). Scan rates of (—) 200 mV/s, (—) 100 mV/s, and (—) mV/s were used and the fifth scan is shown.*

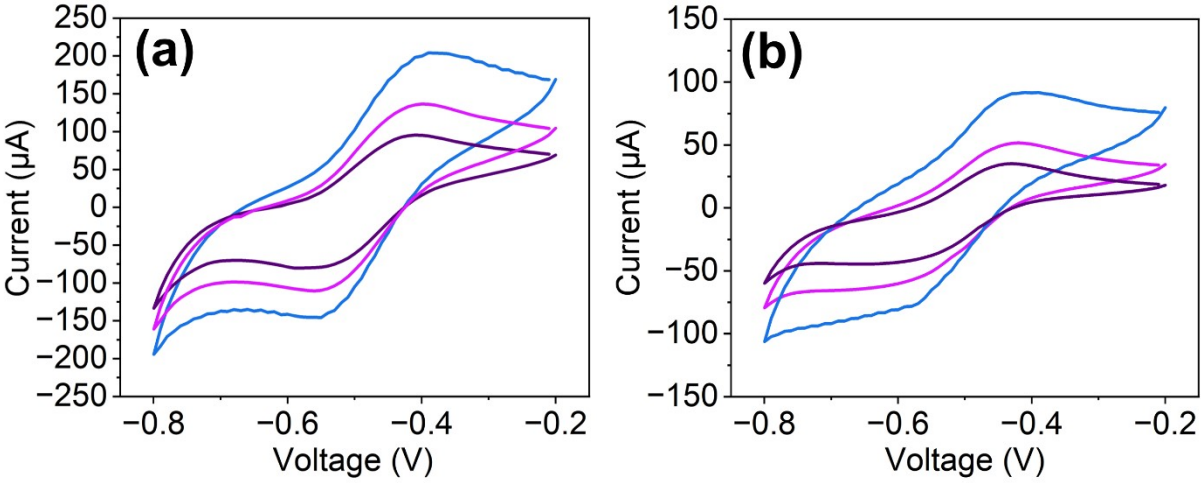


*Figure S12: CV measurement of 0.5 mg/mL **NDI-M** solution at **(a)** pH 6 and **(b)** pH 9 (vs Ag/AgCl). Scan rates of (—) 200 mV/s, (—) 100 mV/s, and (—) 50 mV/s were used and the fifth scan is shown.*

3.2.2 Absorption Spectroscopy

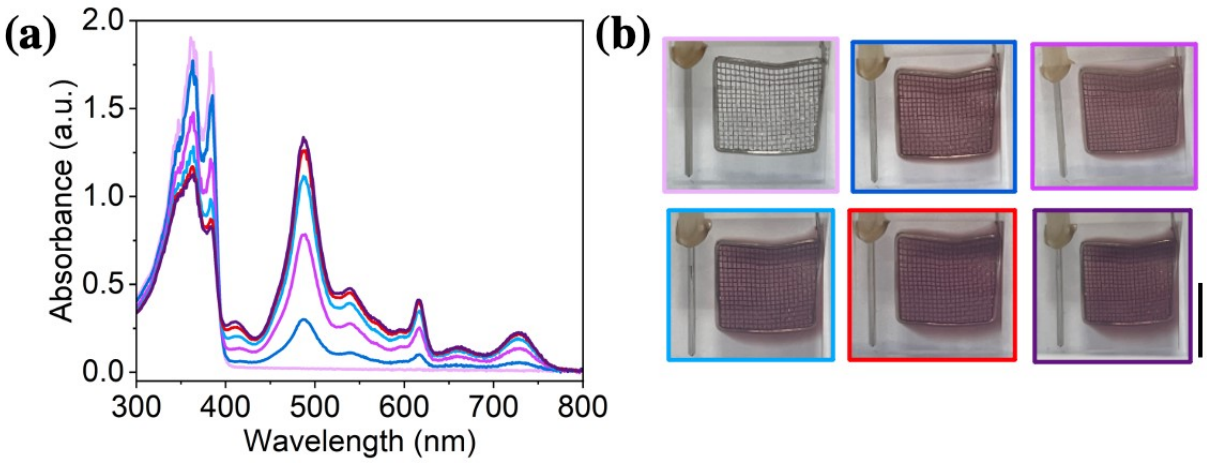


Figure S13: (a) *Absorbance of 0.5 mg/mL* ***NDI-L*** *solution adjusted to pH 6 (—) prior to the application of a potential, and after application of -0.56 V for (—) 4 minutes, (—) 8 minutes, (—)12 minutes, (—)16 minutes, and (—) 20 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 10 mm.*

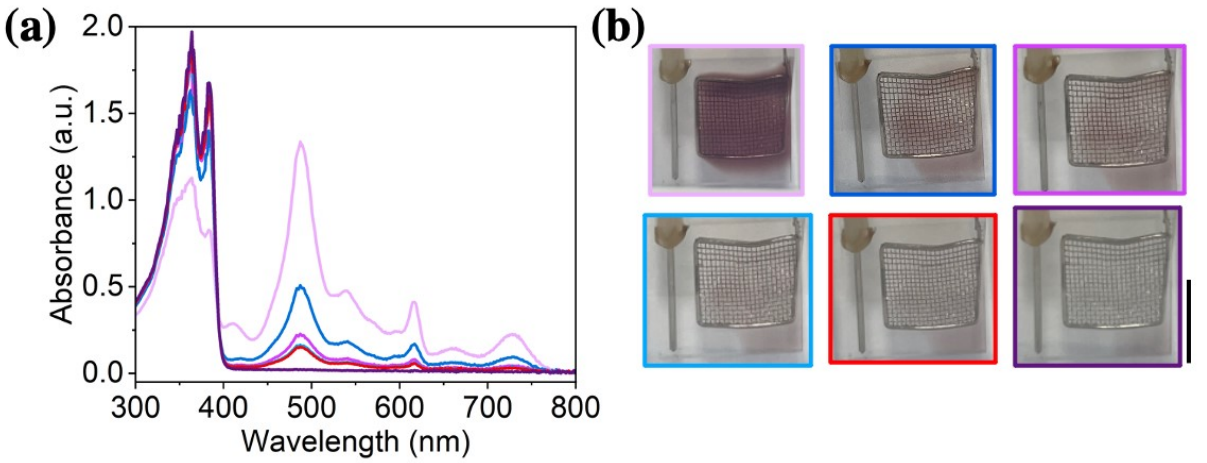


Figure 14: (a) *Absorbance of 0.5 mg/mL* ***NDI-L*** *solution adjusted to pH 6 after (—) the application of –0.56 V for 20 minutes, and after application of -0.45 V for (—) 10 minutes, (—) 20 minutes, (—) 30 minutes, and (—) 40 minutes. The sample was allowed to oxidise in air for an additional (—) 10 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 10 mm.*

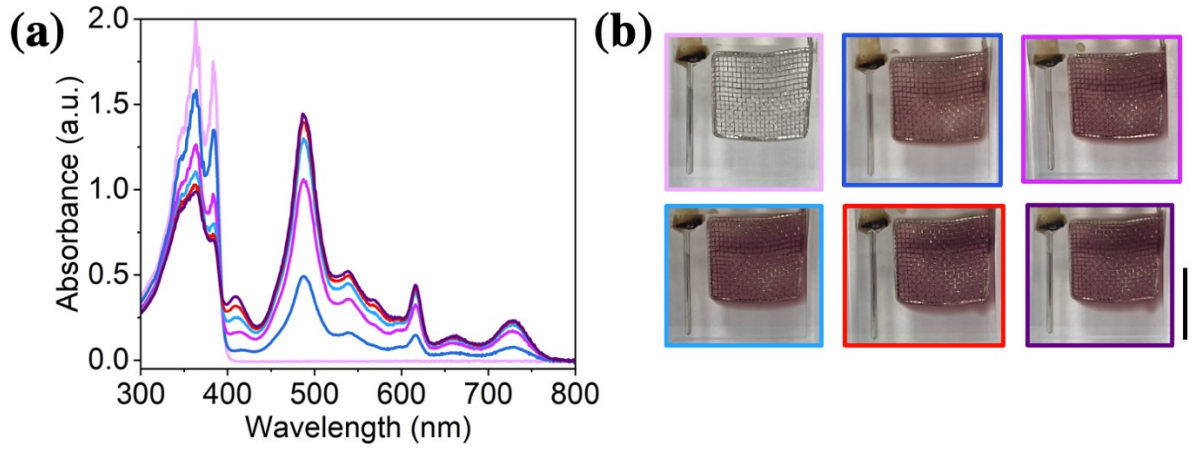


Figure S15: ***(a)*** *Absorbance of 0.5 mg/mL* ***NDI-L*** *solution adjusted to pH 6 (—) prior to the application of a potential, and after application of -0.55 V for (—) 4 minutes, (—) 8 minutes, (—)12 minutes, (—)16 minutes, and (—) 20 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 10 mm.*

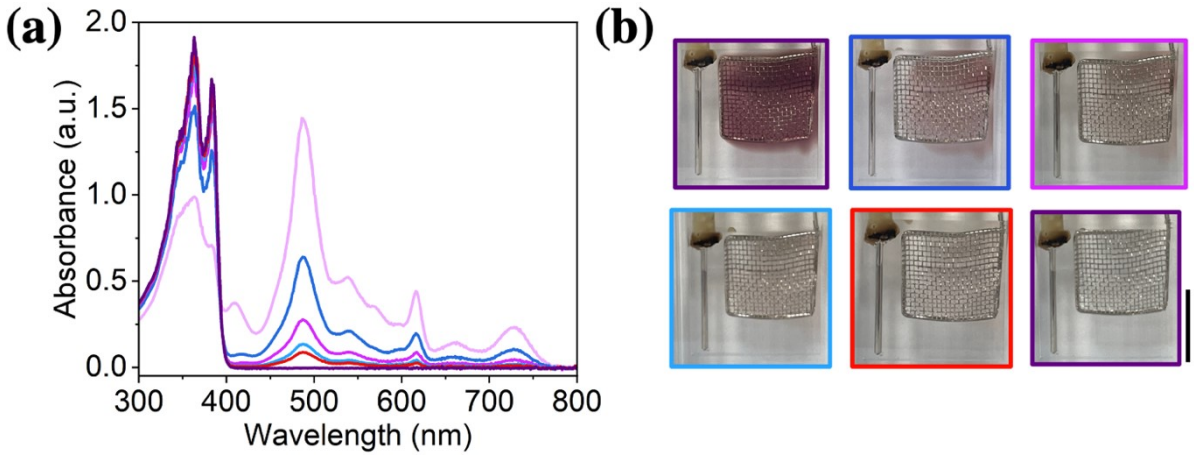


Figure S16: ***(a)*** *Absorbance of 0.5 mg/mL* ***NDI-L*** *solution adjusted to pH 6 after (—) the application of –0.56 V for 20 minutes, and after application of -0.43 V for (—) 10 minutes, (—) 20 minutes, (—) 30 minutes, and (—) 40 minutes. The sample was allowed to oxidise in air for an additional (—) 10 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 10 mm.*

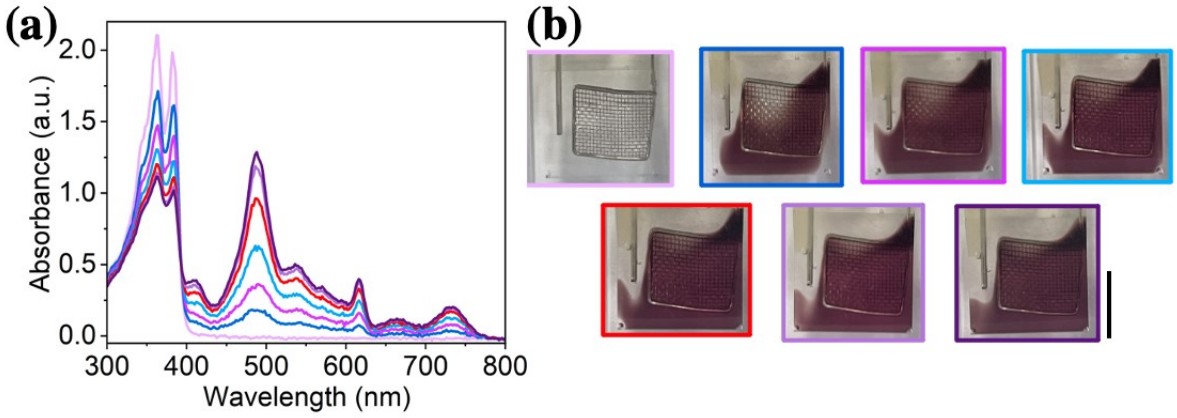


Figure S17: ***(a)*** *Absorbance of 0.5 mg/mL* ***NDI-M*** *solution adjusted to pH 6 (—) prior to the application of a potential, and after application of -0.55 V for (—) 10 minutes, (—) 20 minutes, (—)30 minutes, (—) 40 minutes, (—) 50 minutes and (—) 60 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 5 mm.*

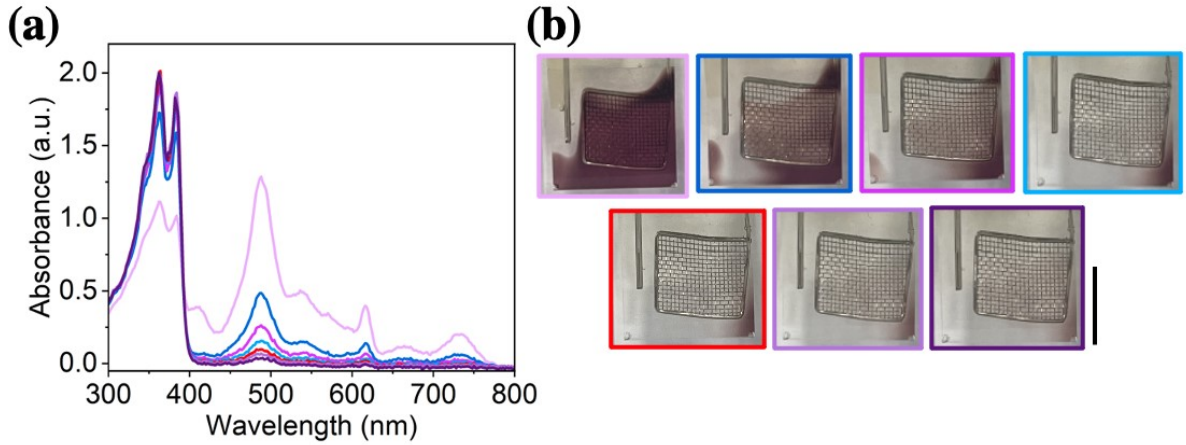


Figure S18: ***(a)*** *Absorbance of 0.5 mg/mL* ***NDI-M*** *solution adjusted to pH 6 after (—) the application of –0.55 V for 20 minutes, and after application of -0.40 V for (—) 10 minutes, (—) 20 minutes, (—) 30 minutes, (—) 40 minutes, (—) 50 minutes and (—) 60 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 5 mm.*

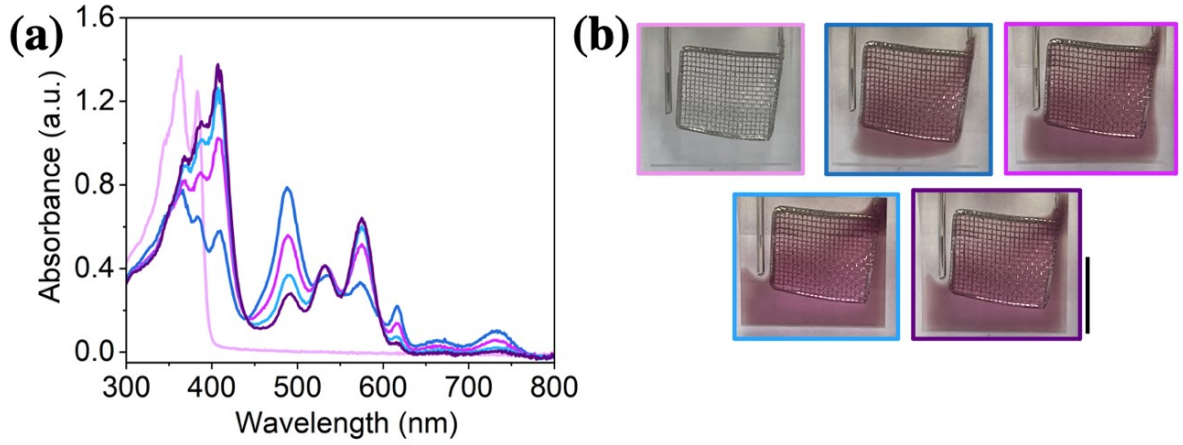


Figure S19: ***(a)*** *Absorbance spectra of 0.5 mg/mL* ***NDI-M*** *solution adjusted to pH 9 (—) prior to the application of a potential, and after application of -0.60 V for (—) 5 minutes, (—) 10 minutes, (—)15 minutes, and (—) 20 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 5 mm*.

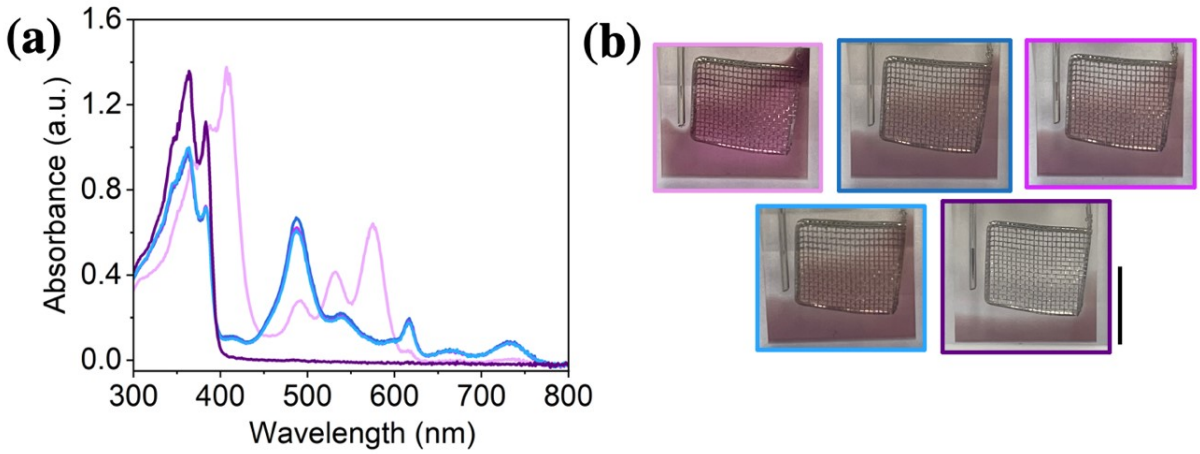


Figure S20: ***(a)*** *Absorbance spectra of 0.5 mg/mL* ***NDI-M*** *solution adjusted to pH 9 after (—) the application of –0.60 V for 20 minutes, and after application of -0.40 V for (—) 10 minutes, (—) 20 minutes, and (—) 30 minutes. The sample was allowed to oxidise in air for an additional (—) 10 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 5 mm.*

3.3 Optical Microscopy

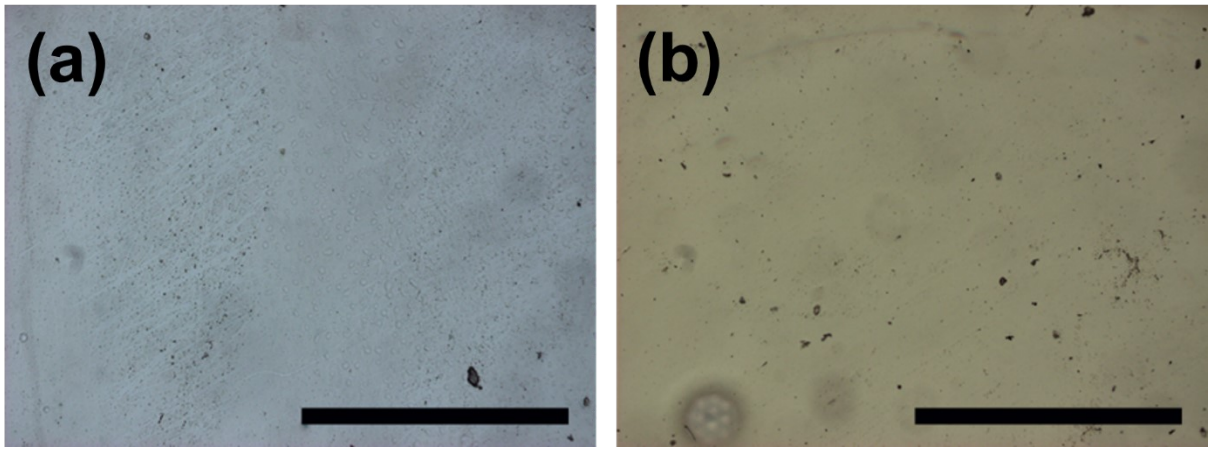


Figure S21: *Optical microscopy images of* ***(a) NDI-L*** *and* ***(b) NDI-M*** *films. Scale bar represents 1.0 mm.*

3.4 Cyclic Voltammetry of Films

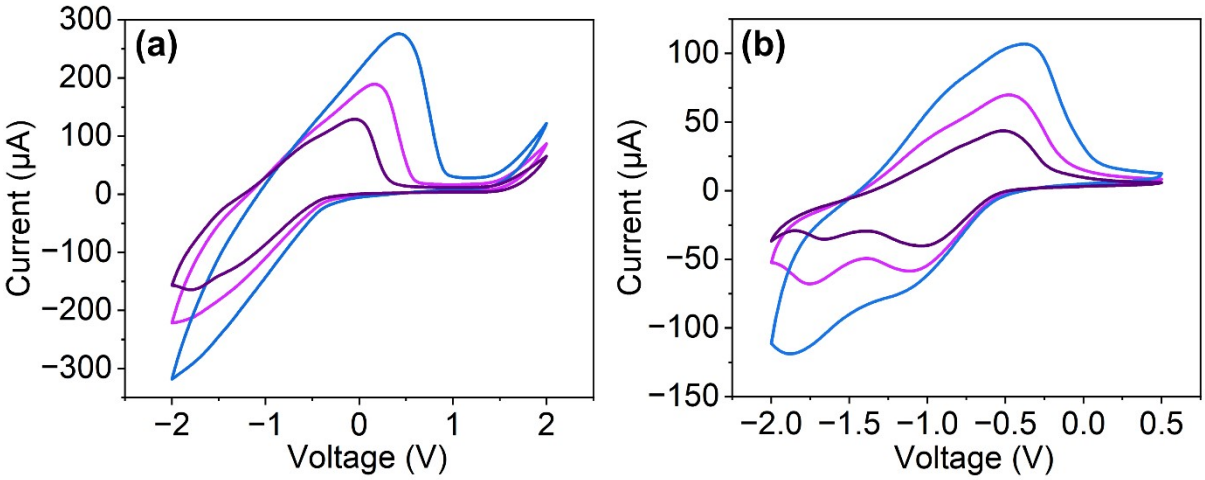


Figure S22: *CV measurement of* ***(a) NDI-L*** *film and* ***(b) NDI-M*** *film, prepared at a pH of 9 and 6, respectively (Vs Ag/$AgNO_3$). Scan rates of (—) 200 mV/s, (—) 100 mV/s, and (—) 50 mV/s were used and the fifth scan is shown.*

3.5 Oxidation of Films

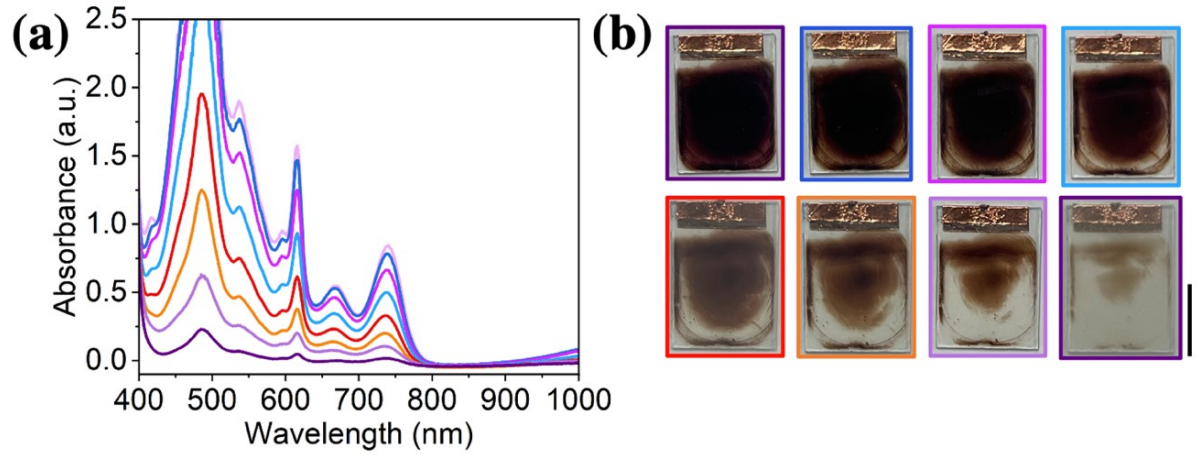


Figure S23: ***(a)*** *Absorbance of* ***NDI-L*** *film after (—) the application of -1.8 V for 20 minutes, and after application of 2.0 V for (—) 10 seconds, (—) 30 seconds, (—) 1 minute, (—) 5 minutes, (—) 10 minutes, (—) 20 minutes, (—) 60 minutes.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 10 mm.*

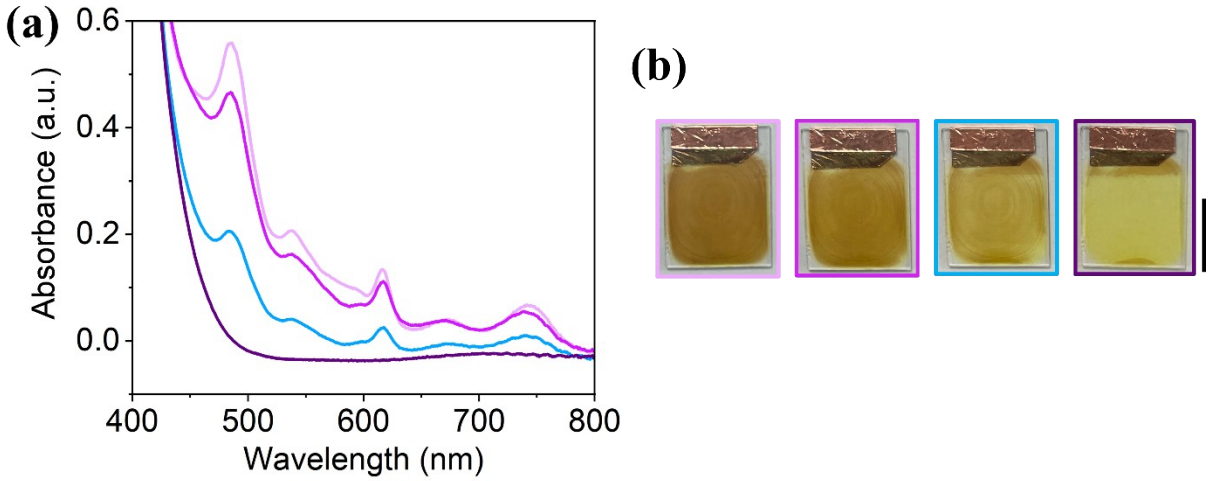


Figure S24: ***(a)*** *Absorbance of* ***NDI-M*** *film after (—) the application of -1.8 V for 20 minutes, and after application of 2.0 V for (—) 10 seconds, (—) 30 seconds minutes, and (—) 1 minute.* ***(b)*** *Photographs taken at corresponding times. Scale bar represents 10 mm.*

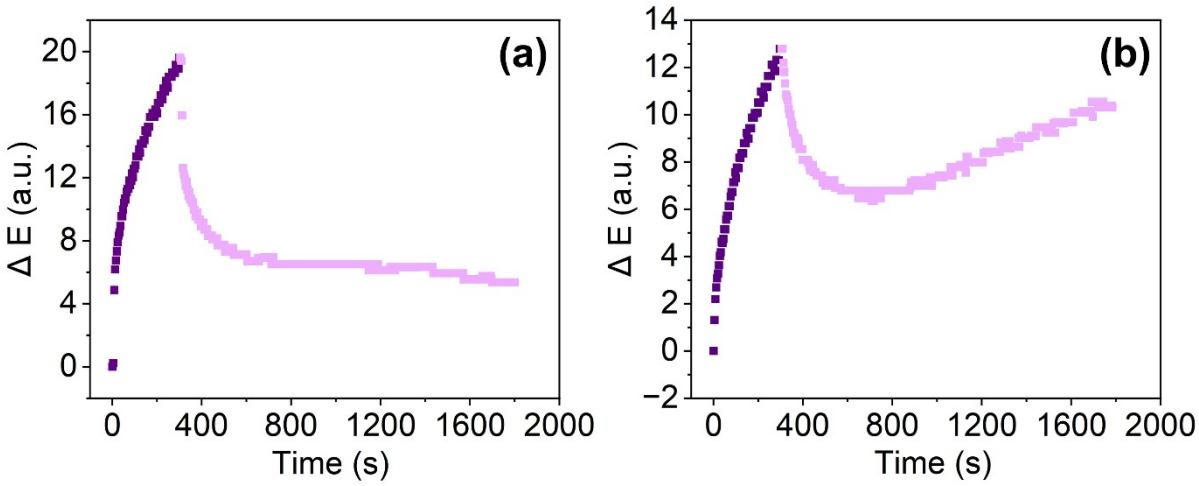


*Figure S25: ΔE of **(a) NDI-L** and (b) **NDI-M** film over time upon application of (■) -1.8 V for 5 minutes and (■) 2.0 V for 25 minutes.*

3.6 Photochromic Response

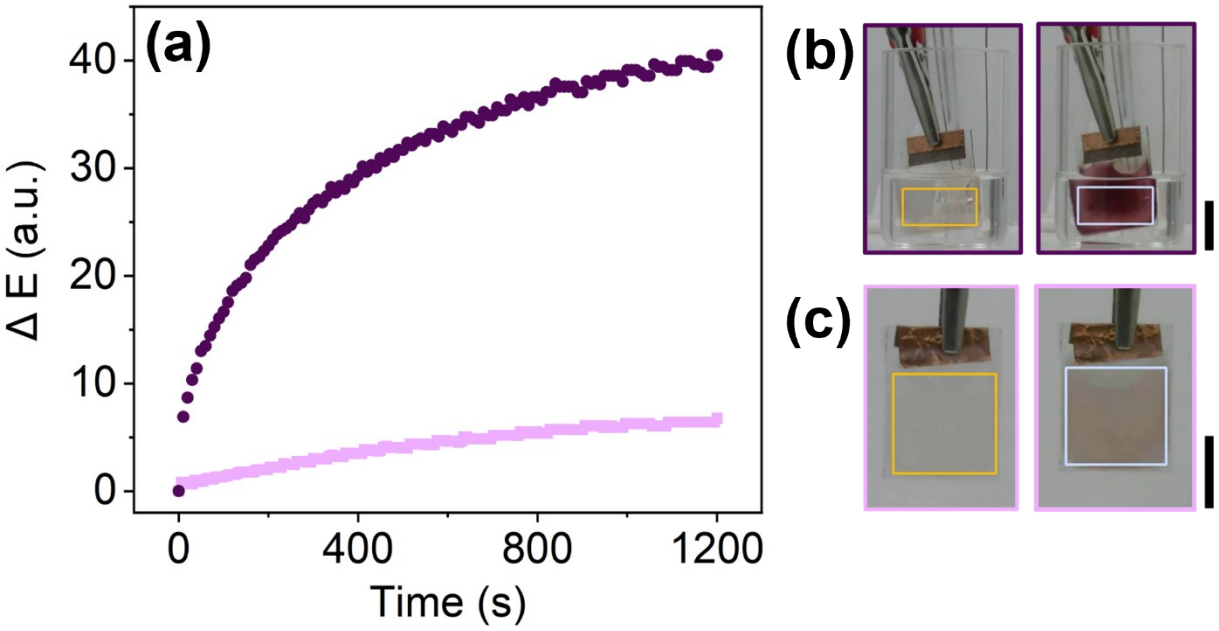


*Figure S26: **(a)** ΔE of **NDI-L** film over time upon electrochemical (■) or photochemical (■) reduction. **(b)** Photographs taken film prior to (left) and after (right) application of -1.8 V for 20 minutes. **(c)** Photographs taken of film after 0 minutes (left) and after 20 minutes (right) inside the lightbox. Scale bar represents 10 mm.*

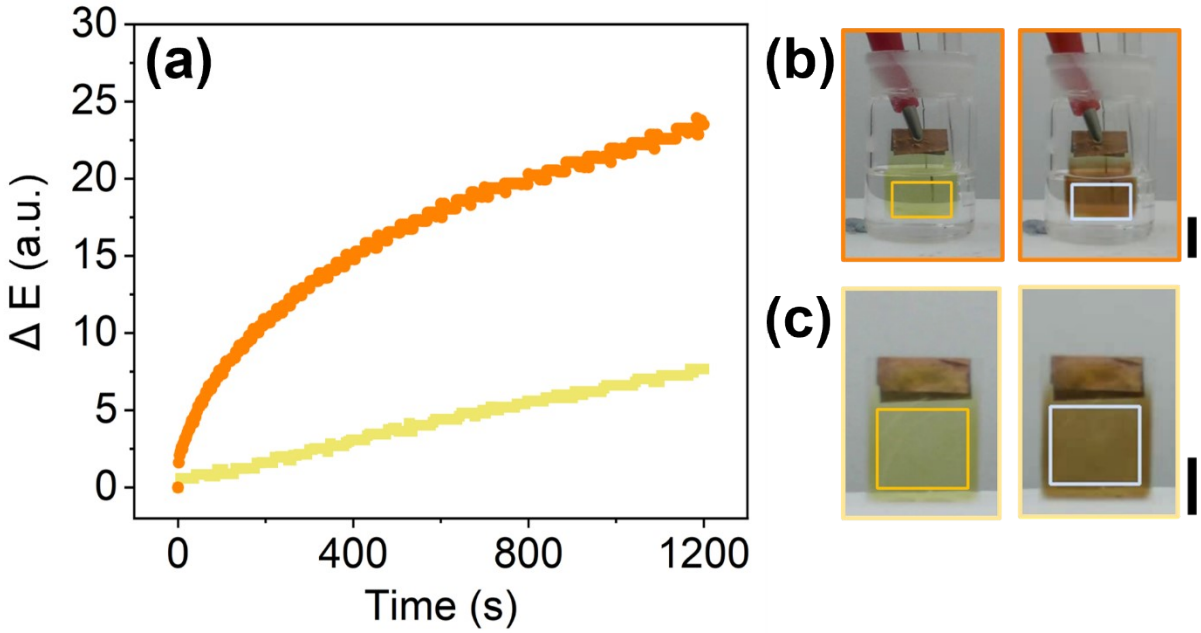


Figure S27: ***(a)*** *ΔE of* ***NDI-M*** *film over time upon electrochemical (■) or photochemical (■) reduction.* ***(b)*** *Photographs taken film prior to (left) and after (right) application of -1.8 V for 20 minutes.* ***(c)*** *Photographs taken of film after 0 minutes (left) and after 20 minutes (right) inside the lightbox. Scale bar represents 10 mm.*

3.7 Open Bench Response

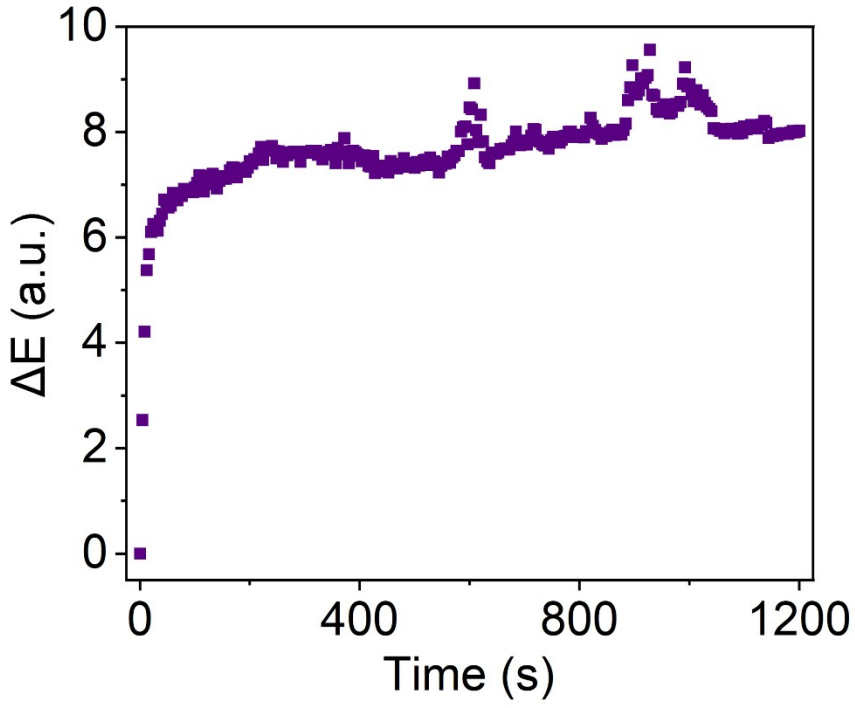


*Figure S28: ΔE of **NDI-L** film over time upon electrochemical reduction in uncontrolled lighting environment.*

3.8 Electrochromic Response of PBI-L Films

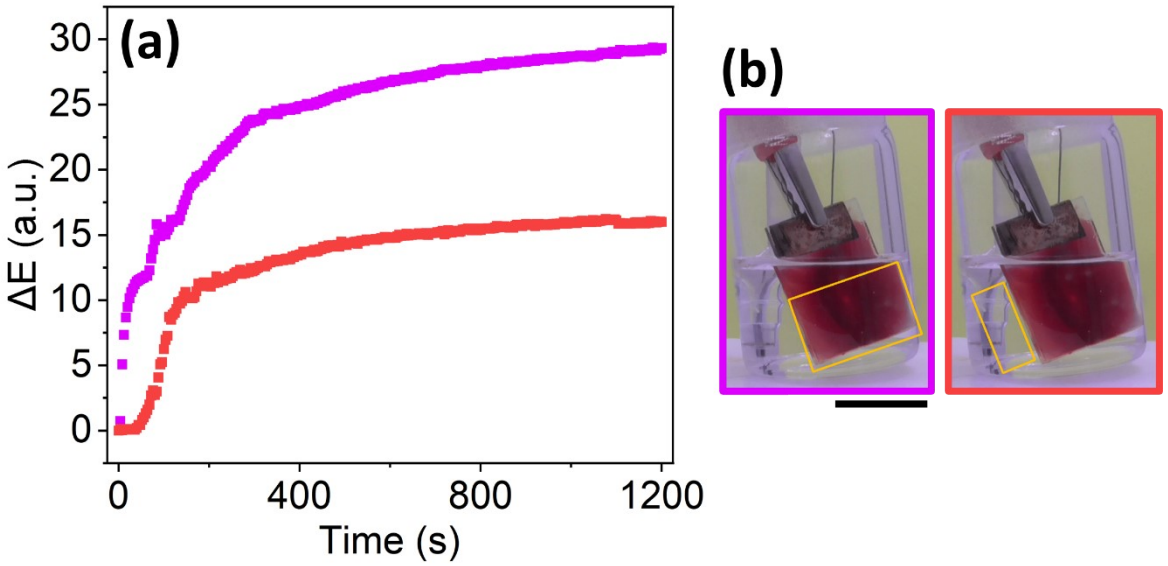


*Figure S29: **(a)** ΔE of (■) **PBI-L** film and (■) electrolyte solution upon application of -1.8 V for 20 minutes. **(b)** Area of (left) film and (right) electrolyte solution measured by Kineticolor. Scale bar is for 15 mm.*

3.9 HSV/LAB Measurements

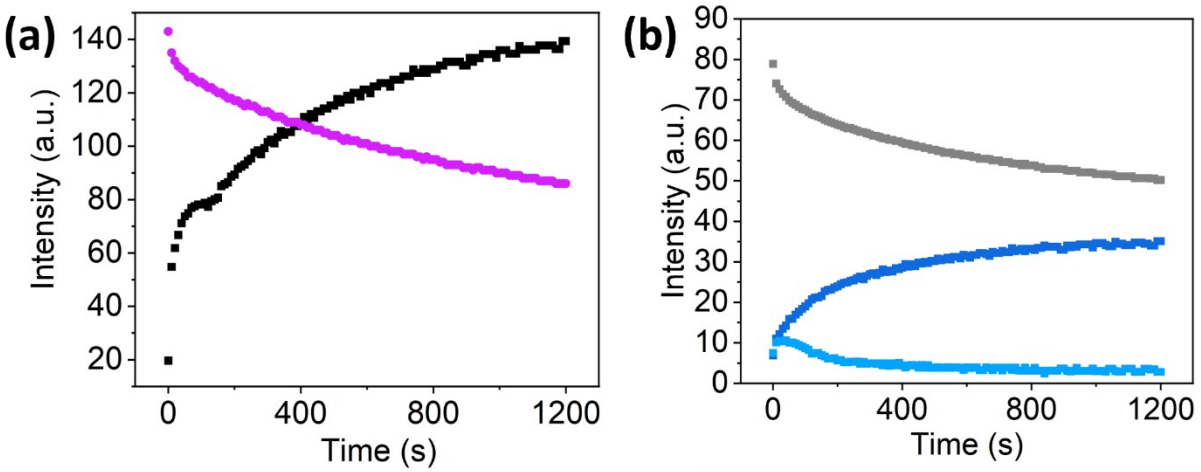


*Figure S30: Variations in colour space of **NDI-L** film over time upon application of -1.8 V for 20 minutes. **(a)** HSV plot showing intensity saturation (■) and value (■) of*

film. ***(c)*** *LAB plot showing intensity of lightness (■), a component (■), and b component (■) of film.*

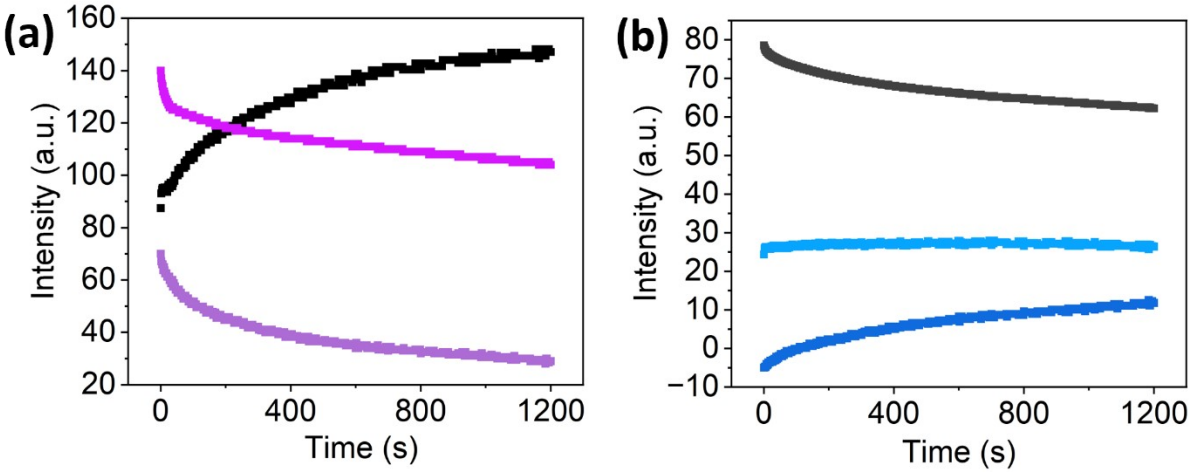


Figure S31: *Variations in colour space of* ***NDI-M*** *film over time upon application of -1.8 V for 20 minutes.* ***(a)*** *HSV plot showing intensity of hue (■), saturation (■) and value (■) of film.* ***(c)*** *LAB plot showing intensity of lightness (■), a component (■), and b component (■) of film.*

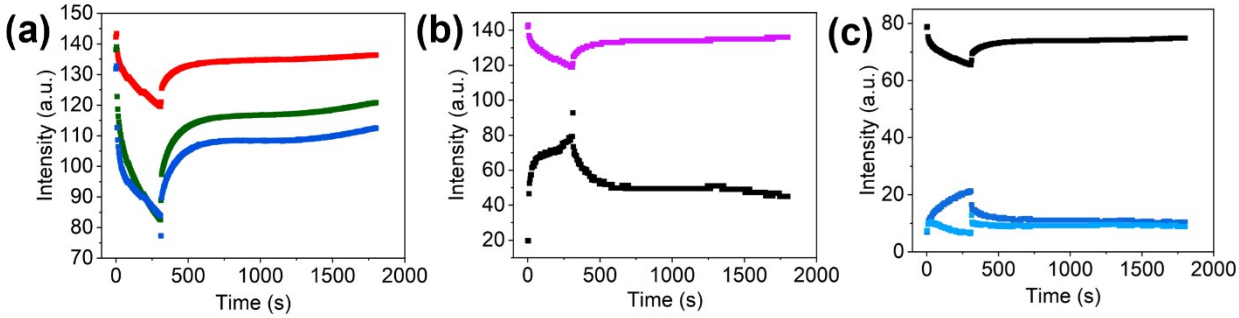


Figure S32: *Variations in colour space of* ***NDI-L*** *film over time upon application of -1.8 V for 5 minutes and 2.0 V for 25 minutes.* ***(a)*** *RGB plot showing intensity of red (■), green (■), and blue.* ***(b)*** *HSV plot showing intensity of saturation (■) and value (■) of film.* ***(c)*** *LAB plot showing intensity of lightness (■), a component (■), and b component (■) of film.*

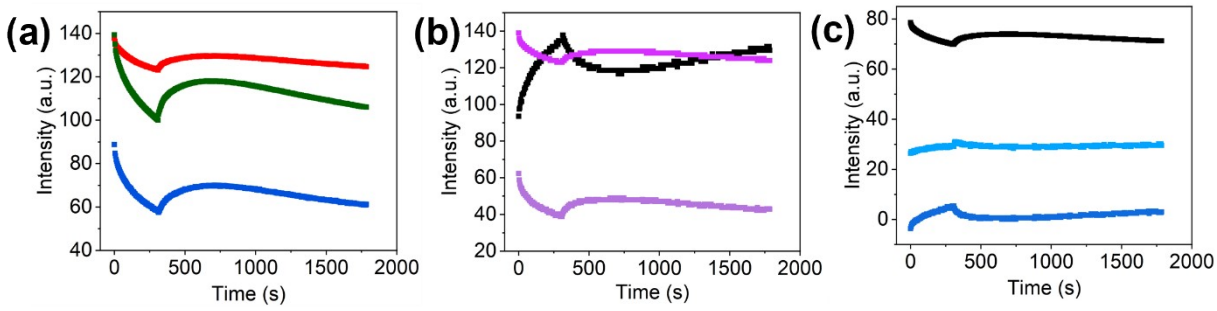


*Figure S33: Variations in colour space of **NDI-M** film over time upon application of -1.8 V for 5 minutes and 2.0 V for 25 minutes. **(a)** RGB plot showing intensity of red (■), green (■), and blue. **(b)** HSV plot showing intensity of hue (■), saturation (■) and value (■) of film. **(c)** LAB plot showing intensity of lightness (■), a component (■), and b component (■) of film.*

3.10 Extended Electronic Reduction

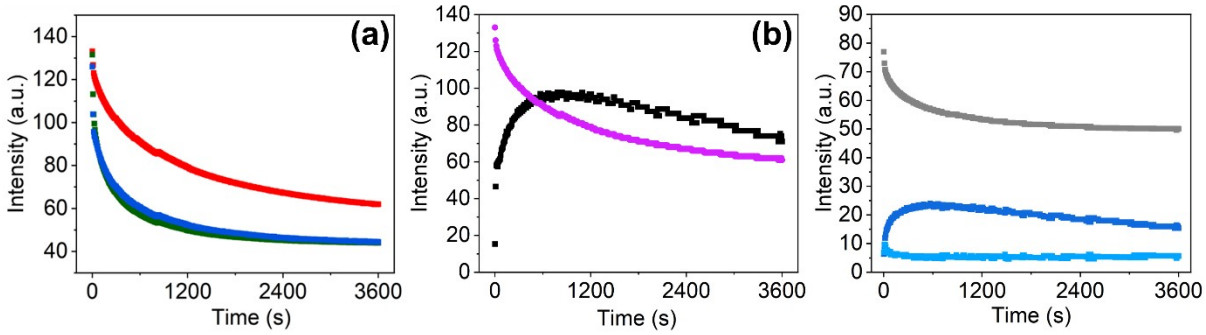


*Figure S34: Variations in colour space of **NDI-L** film over time upon application of -1.8 V for 60 minutes. **(a)** RGB plot showing intensity of red (■), green (■), and blue (■). **(b)** HSV plot showing intensity of hue (■), saturation (■) and value (■). **(c)** LAB plot showing intensity of lightness (■), a component (■), and b component (■).*

3.11 Colouration Homogeneity

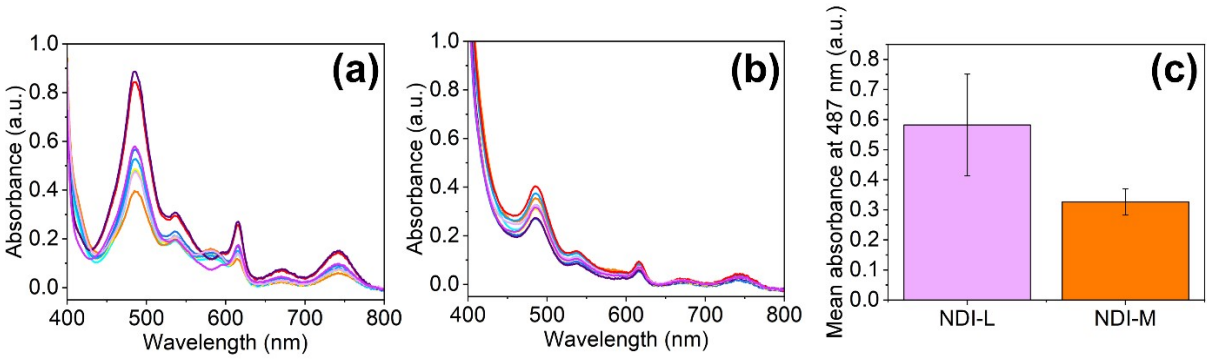


Figure S35: *Absorbance of* ***(a) NDI-L*** *and* ***(b) NDI-M*** *film following application of -1.8 V for 20 minutes. A total of 9 measurements were performed on each film across different areas.* ***(c)*** *Mean absorbance at 487 nm following reduction. Error bars represent standard deviation.*

3.12 Texture Derived Analysis

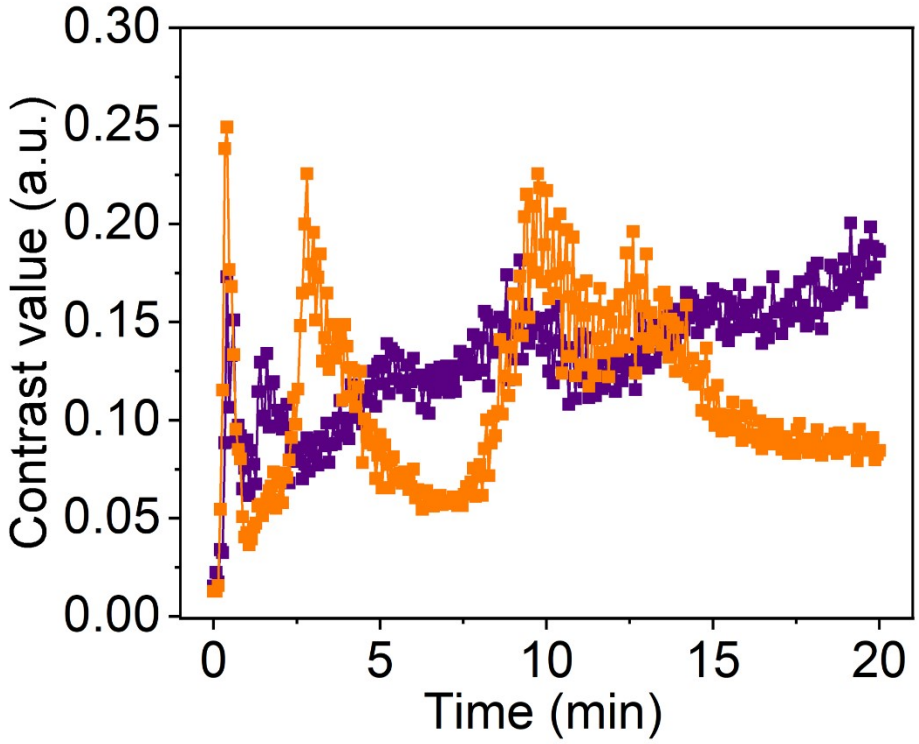


Figure S36: *Contrast of* ***NDI-L*** *(■) and* ***NDI-M*** *(■) films over time upon electrochemical reduction.*

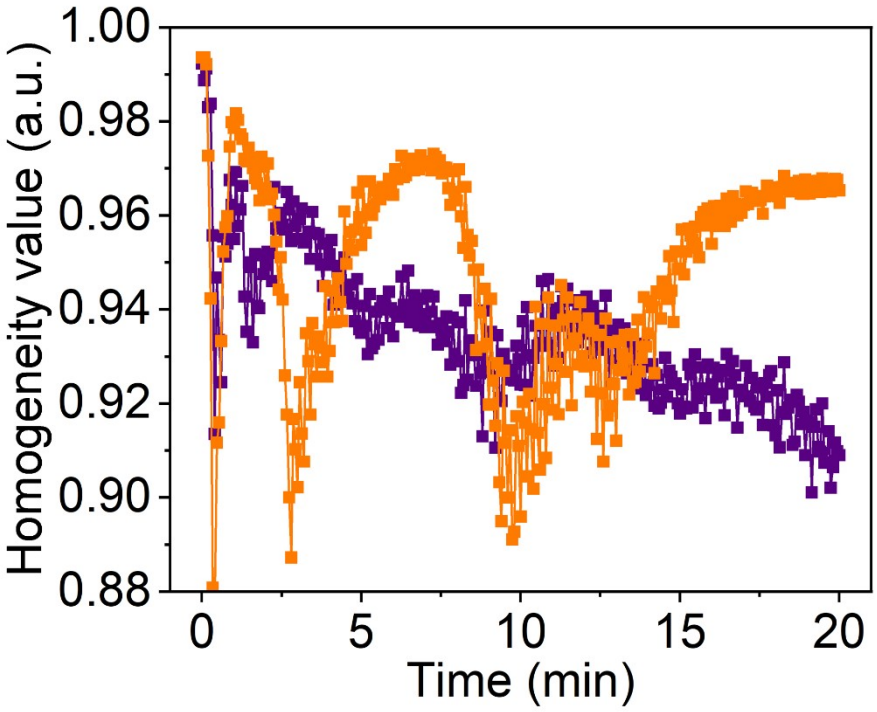
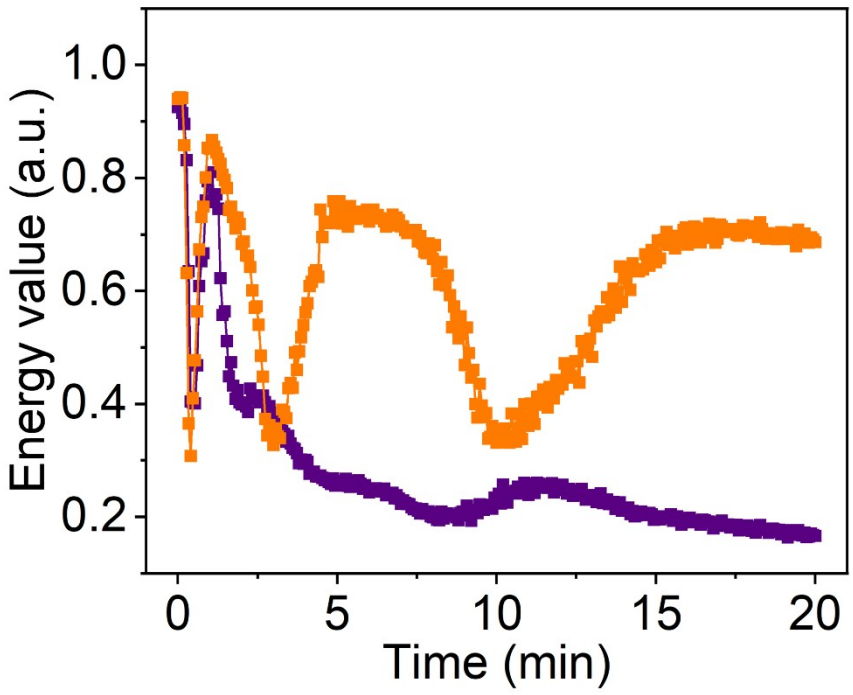


Figure S37: *Homogeneity of* ***NDI-L*** *(■) and* ***NDI-M*** *(■) films over time upon*



electrochemical reduction.

Figure S38: *Energy of* ***NDI-L*** *(■) and* ***NDI-M*** *(■) films over time upon electrochemical reduction.*

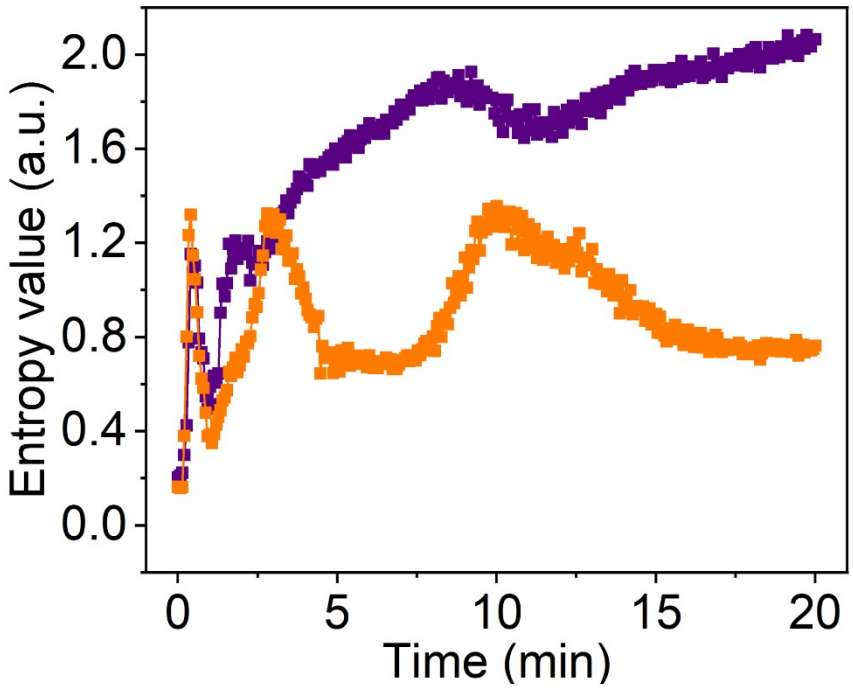


Figure S39: *Entropy of* ***NDI-L*** *(■) and* ***NDI-M*** *(■) films over time upon electrochemical reduction*

3.13 Cyclability

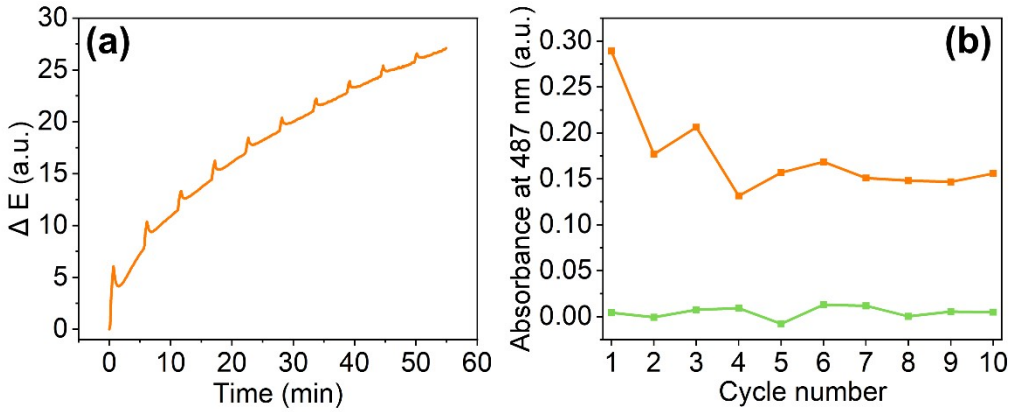


Figure S40: *ΔE of* ***NDI-M*** *film throughout 10 redox cycles. Films were reduced via application of -1.8 V for 30 seconds and oxidised via application of 1.6 V for 5 minutes.* ***(b)*** *Absorbance at 485 nm of* ***NDI-M*** *film throughout 10 redox cycles. Films were reduced via application of -1.8 V for 30 seconds and oxidised via*

application of 2.0 V for 5 minutes. Orange line shows the absorbance in the reduced state. Green line shows the absorbance in the oxidised state.

4. References

1. R. I. Randle, L. Cavalcanti, S. Sproules and E. R. Draper, *Mater. Adv.*, 2022, **3**, 3326–3331.

2. L. Thomson, R. E. Ginesi, D. D. Osborne, E. R. Draper and D. J. Adams, *Chem. Eur. J.*, 2023, **29**, e202300663.

3.. M. Fabretto, T. Vaithianathan, C. Hall, P. Murphy, P. C. Innis, J. Mazurkiewicz and G. G. Wallace, *Electrochem. Commun.*, 2007, **9**, 2032–2036.