Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

Polyiodide solid-state dye-sensitized solar cell produced from a standard liquid I^-/I_3^- electrolyte

Ellie Tanaka[a] and Neil Robertson*[a]

a. *The University of Edinburgh School of Chemistry, David Brewster Road, Edinburgh EH9 3FJ, UK.*

Contents:

Experimental 1 Variation of fabrication procedures of Liq-I/Ply-I DSSCs.
Fig. S1 *J-V* curves of Liq-I/Ply-I DSSCs using different dyes and binding methods.
Fig. S2 Statistical performance of the Liq-I/Ply-I DSSCs using 5T dye.
Fig. S3 *J-V* curves of the best Ply-I (stb.) DSSC, measured with a 0.0625 cm^2 aperture.
Table S1 Performance values in Fig. S3.
Fig. S4 Calculation of the cell lifetime.
Fig. S5 Transient photocurrent of Liq-I/Ply-I DSSC.
Fig. S6 Optical images of mask silhouette.
Fig. S7 *J-V* curve of Ply-I DSSC with no dye attached to the TiO_2.
Fig. S8 Tauc plots to determine the optical gap of Liq-I and Ply-I.
Fig. S9 XRD pattern of Ply-I.
Fig. S10 Molecular structures of the electrolyte species; Raman spectra of *t*BP and MeCN.
Fig. S11 Images of I_2 + DMPII and I_2 + LiI_2 left outside for a few days; Raman spectra of I_2 + DMPII and I_2 + LiI_2.
Table S2 Peak assignment in the IR spectra (Fig. 7).
Fig. S12 FIB-SEM of Ply-I DSSC cross section.
Fig. S13 Images of Liq-I and Ply-I DSSC, *J-V* curves to show weak contact between Pt and dyed TiO_2.
Fig. S14 Raman spectra of substance obtained from Liq-I dried at different speeds.
Fig. S15 Bode plots of Liq-I; Ply-I (peak) and Ply-I (stb.) DSSCs.
Fig. S16 Equivalent circuit for the EIS fitting.

Variation of fabrication procedures of Liq-I/Ply-I DSSCs.

Dye bath:

N719 dye:[1] 0.5 mM N719 in ethanol with 5 mM chenodeoxycholic acid (CDCA). Thickness of the TiO_2 film was ~20 µm.

D149 dye:[2] 0.5 mM D149 in acetonitrile/*t*-butanol (1:1, v/v) with 1 mM CDCA. The thickness of the TiO_2 film was ~16 µm.

SQ2 dye:[3] 0.3 mM SQ2 in acetonitrile/*n*-butanol (17:3, v/v) with 3 mM CDCA. The thickness of the TiO_2 film was ~8 µm.

Spacer:

Surlyn: A 25-µm thick Surlyn (DuPont) sheet was inserted between the anode and cathode for perfect insulation. The sandwich-assembly was placed on a hotplate at 125 °C, where the Surlyn was melt by applying pressure from the top to ensure complete sealing.

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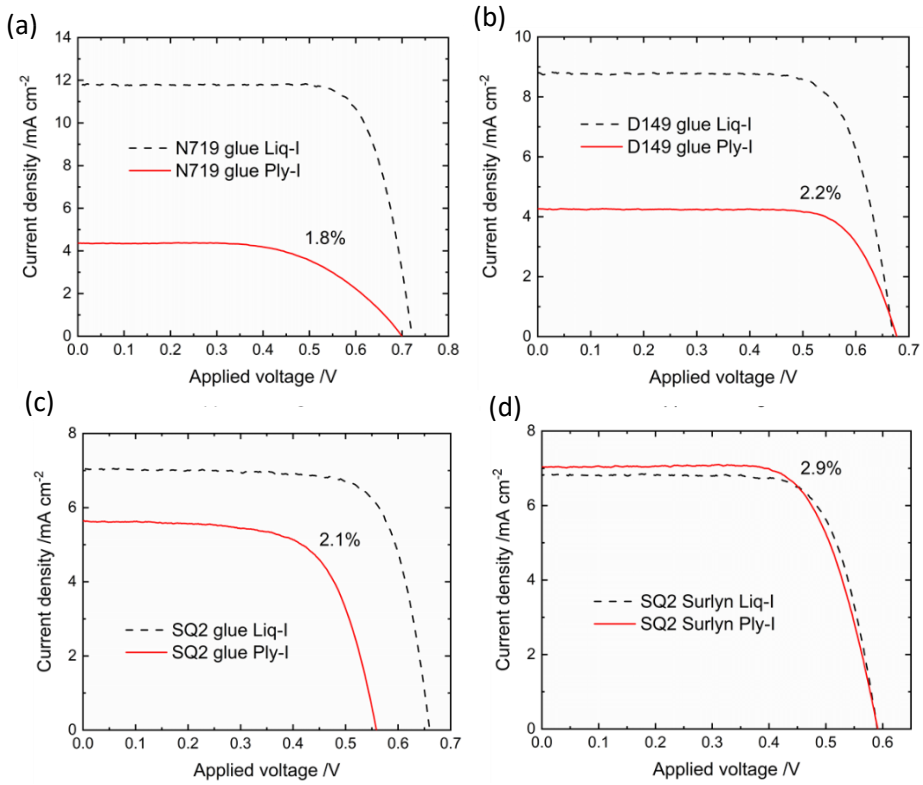

Fig. S1 *J-V* curves of Ply-I DSSCs with a variation of dyes and spacers. The cells were measured at 1 sun with an aperture of 0.126 cm^2. The percentage value in each panel denotes the PCE of the Ply-I DSSC.

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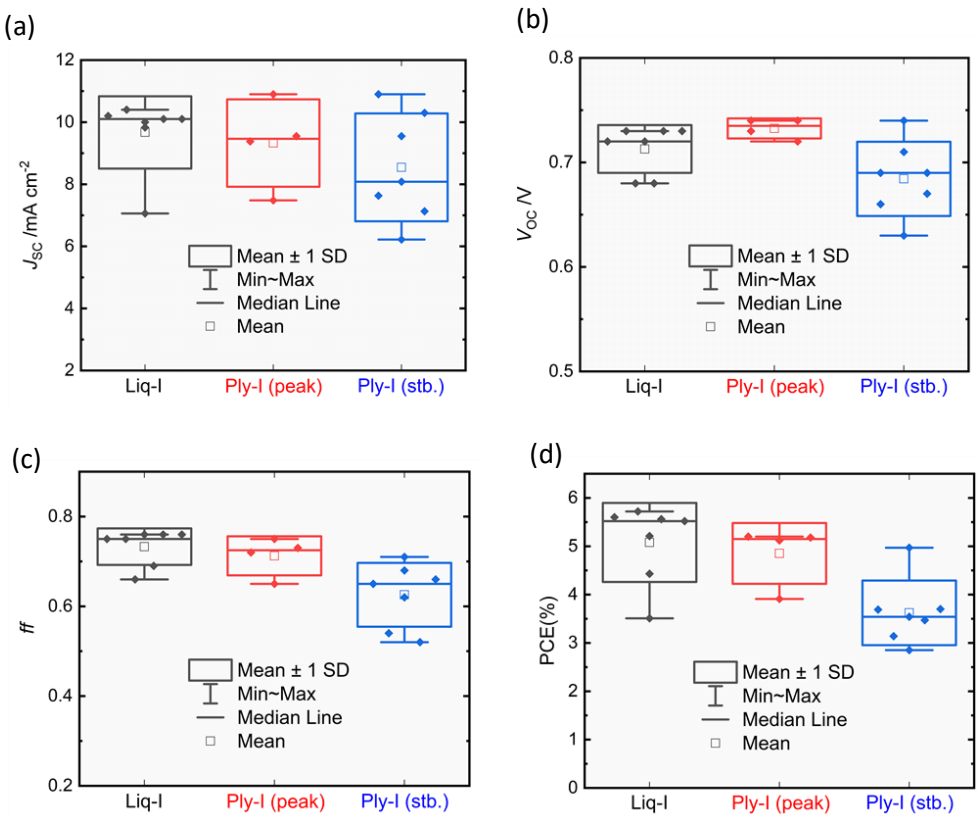

Fig. S2 Statistics of the photovoltaic parameters of sealed Liq-I DSSCs and unsealed Ply-I DSSCs (peak and stb.). The cells numbered from four to seven and were tested with an aperture of 0.126 cm^2.

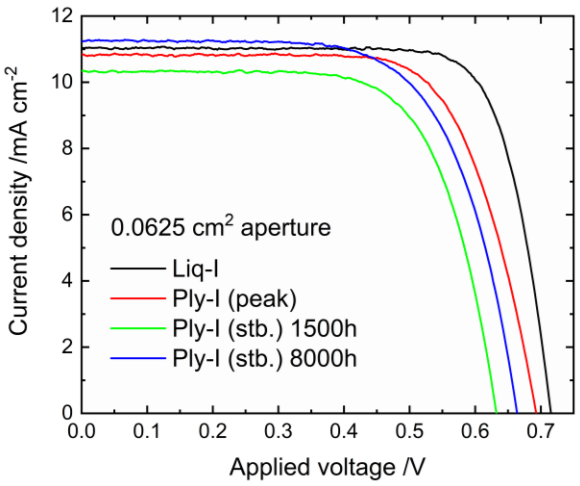

Fig. S3 *J-V* curves of the best Ply-I (stb.) DSSC at the different stages of drying/evolution, measured with a 0.0625 cm^2 aperture: before drying (Liq-I, t = 0); after 170 h (Ply-I (peak)); after 1500h (Ply-I (stb.) 1500h) and after 8000 h (Ply-I (stb.) 8000h).

Table S1 Photovoltaic characteristics of the best Ply-I (stb.) DSSC at 0h (Liq-I), 120 h (Ply-I (peak)), 1500 h and 1800 h (Ply-I (stb.) using a 0.0625 cm^2 aperture.

With 0.0625 cm^2	J_{SC}/mA cm^{-2}	V_{OC}/V	ff	PCE (%)
Liq-I	11.0	0.71	0.78	6.1
Ply-I (peak)	10.8	0.70	0.71	5.3
Ply-I (stb.) 1500 h	10.3	0.63	0.69	4.5
Ply-I (stb.) 8000 h	11.3	0.66	0.67	5.0

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Calculation of T_{80} and T_{S80}

The lifetime of the best Ply-I (stb.) DSSC was estimated from fitted linear curves shown in Fig. S4.

The red square plots (0.0625 cm^2 square aperture) from 600 h to 3200 h and red circle plots (0.126 cm^2 circular aperture) from 1000 h to 3200 h in Fig. 3 (d) were used.

Fitting conditions: Non-weighted least-squares linear fitting with intercept non-fixed.

1) T_{80} and T_{S80} for 0.0625 cm^2:

T_{80}: time until 20% PCE drop from $T = 0$

Equation of fitted curve: $y = - 6.48966 \cdot 10^{-5} x + 4.71933$ (with intercept at $T = 0$)

By entering $y = 0.8 \times 4.71933$, $x = 14544$ h …T_{80}

T_{S80}: time until 20% PCE drop from $T_S = 0$ (T + 600 h)

Equation of fitted curve: $y = - 6.48966 \cdot 10^{-5} x + 4.65443$ (with intercept at $T_S = 0$)

By entering $y = 0.8 \times 4.65443$, $x = 14344$ h …T_{S80}

2) T_{80} and T_{S80} for 0.126 cm^2:

T_{80}: time until 20% PCE drop from $T = 0$

Equation of fitted curve: $y = - 1.96107 \cdot 10^{-4} x + 4.42842$ (with intercept at $T = 0$)

By entering $y = 0.8 \times 4.42842$, $x = 4516$ h …T_{80}

T_{S80}: time until 20% PCE drop from $T_S = 0$ (T + 1008 h)

Equation of fitted curve: $y = - 1.96107 \cdot 10^{-4} x + 4.23074$ (with intercept at $T_S = 0$)

By entering $y = 0.8 \times 4.23074$, $x = 4315$ h …T_{S80}

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Calculation of η_{1000} and PCE loss

The PCE loss of the best Ply-I (stb.) DSSC was calculated from the fitted linear curves shown in Fig. S4.

1) η_{1000} for 0.0625 cm^2:

Equation of fitted curve: $y = -6.48966 \cdot 10^{-5} x + 4.65443$ (with intercept at $T_S = 0$)

By entering x = 1000 h, the loss per 1000 h is 0.0648966% PCE

2) η_{1000} for 0.126 cm^2:

Equation of fitted curve: $y = -1.96107 \cdot 10^{-4} x + 4.23074$ (with intercept at $T_S = 0$)

By entering x = 1000 h, the loss per 1000 h is 0.196107% PCE

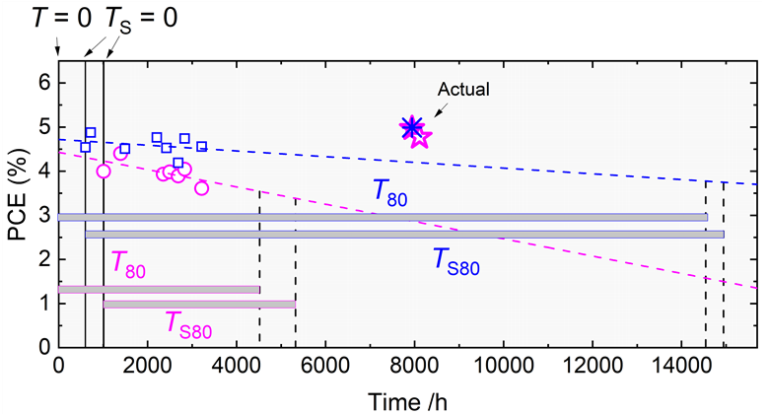

Fig. S4 Extract of the red open square plots and red open circle plots in Fig. 3 (d), with the corresponding fitted linear curves and lifetimes for each method described above. Blue squares: equivalent to the red open squares in Fig. 3 (d). Pink circles: equivalent to the red open circles in Fig. 3 (d). Blue asterisk and pink stars: the experimental values recorded at ~8000 h for the same cell, measured with an aperture of 0.0625 cm^2 and 0.126 cm^2, respectively.

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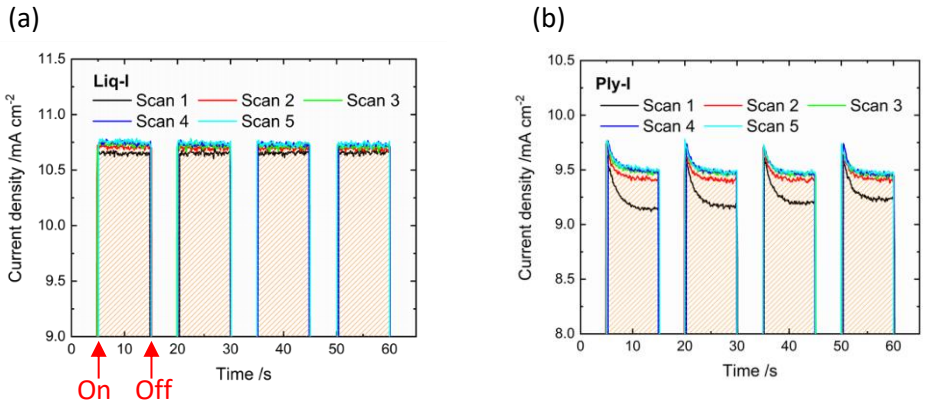

Fig. S5 Transient photocurrent of (a) Liq-I DSSC and (b) Ply-I DSSC at a fixed voltage of 0.4 V, and with an aperture of 0.126 cm^2. The light (1 sun) was switched on and off for 10 s × 4 times with intervals of 5 s for each cycle.

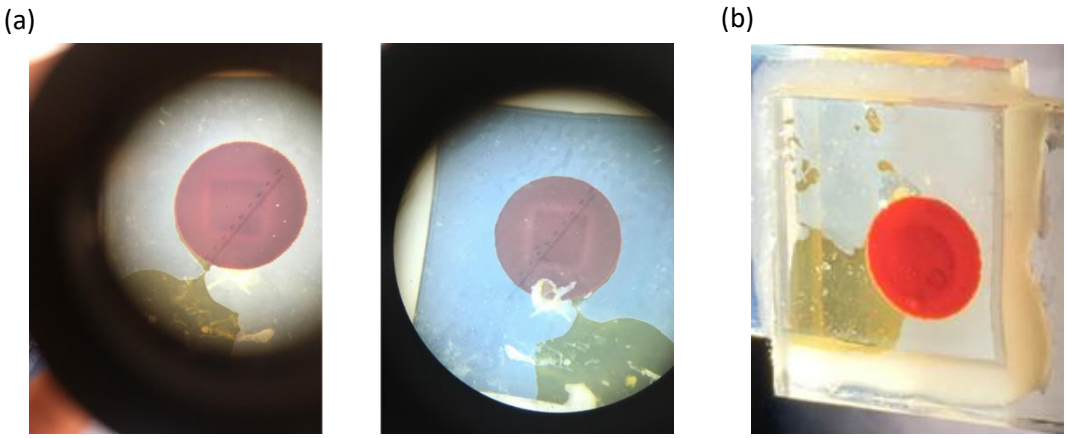

Fig. S6 (a) Optical microscope images of a square mask (a = 2.5 mm, 0.0625 cm^2) silhouette appearing on the active area, taken from the anode side and cathode side. (b) Photograph of a circle mask (d = 4 mm, 0.126 cm^2) silhouette appearing on the active area, taken from the anode side.

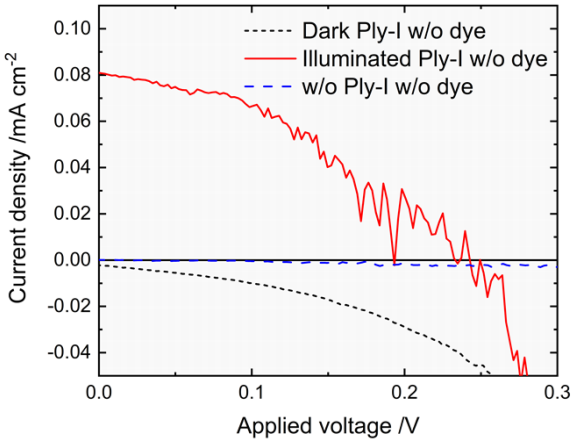

Fig. S7 *J-V* curve of a complete Ply-I DSSC without the use of a dye sensitizer (FTO/c-TiO_2/m-TiO_2/Ply-I/Pt). Rise of a weak photocurrent (0.08 mA cm^{-2}) under 1 sun illumination indicates that the Ply-I itself acts as a "dye" in the Ply-I DSSC.

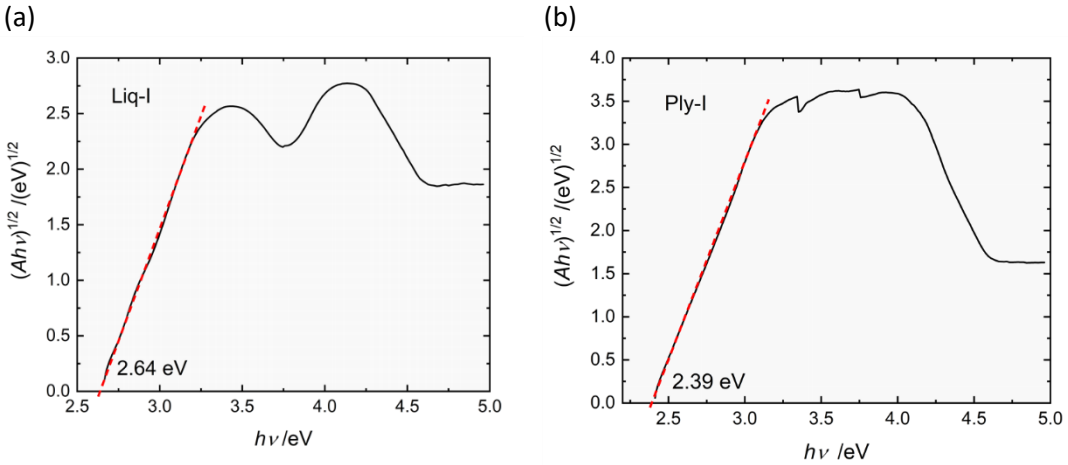

Fig. S8 Tauc plots to estimate the optical gaps of (a) Liq-I and (b) Ply-I from their UV-Vis spectra in Fig. 5. The red dashed lines are the fitted curves.

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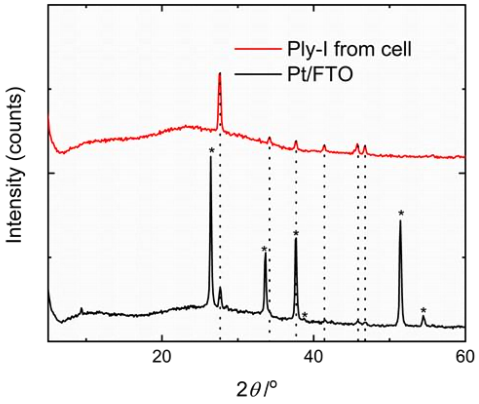

Fig. S9 XRD pattern of Ply-I rubbed onto a glass slide from the cathode side of a freshly opened DSSC. No new peaks are seen besides the Pt peaks, which appear due to the way the sample was prepared. The peaks from Pt/FTO marked with the asterisks (*) are assigned to FTO.

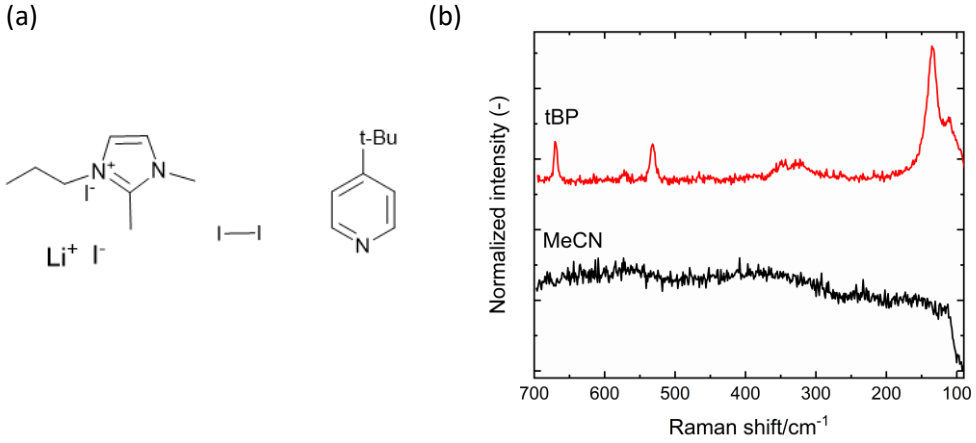

Fig. S10 (a) Molecular structures of the raw materials that compose the I^-/I_3^- electrolyte (Liq-I) in the study. The solvent was anhydrous acetonitrile. (b) Raman spectra of tBP and MeCN.

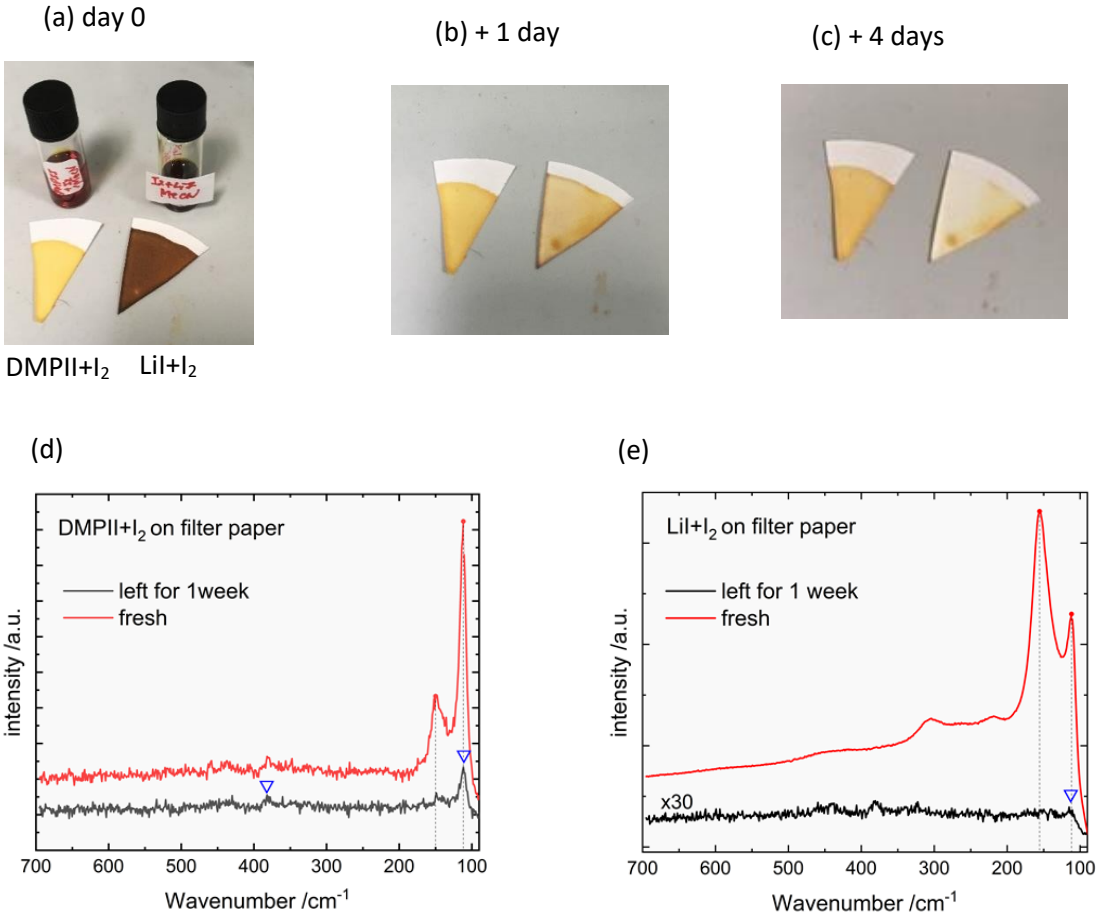

Fig. S11 (a) Fresh DMPII+I2 (left) and LiI+I2 (right) placed on filter paper. (b), (c): The paper left (b) after a day and (c) after 4 days. (d), (e): Raman spectra of (c) DMPII+I_2 and (d) LiI+I_2 placed on filter paper, freshly coated (red) and left for a week (black). The blue triangle indicates the peak overlap with DMPII or LiI.

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Table S2 Assignment of the peaks in the IR spectra in Fig. 7.[4–6]

Wavenumber /cm^{-1}	Symbol	Vibration mode
3756	Asterisk	-OH stretching of H_2O (g)
3600-3200	Filled diamond	-OH stretching of H_2O (l)
3100-3000	Open square	=C-H stretching
2960	Open triangle	-C-H stretching
2349	Asterisk	O=C=O stretching of CO_2 (g)
2250	Filled triangle	-C≡N stretching
1720	Hash	Unknown peak
1600-1630	Filled diamond	H-O-H bending of H_2O (l)
1595	Asterisk	H-O-H bending of H_2O (g)
1450	Filled circle	-CH_3 stretching
1380	Open circle	-CH_3 bending
1030-1540	Open diamond	Unassigned, observed in DMPII+I_2 and Ply-I
750	Filled square	-C-H bending
665	Asterisk	O=C=O bending of CO_2 (g)

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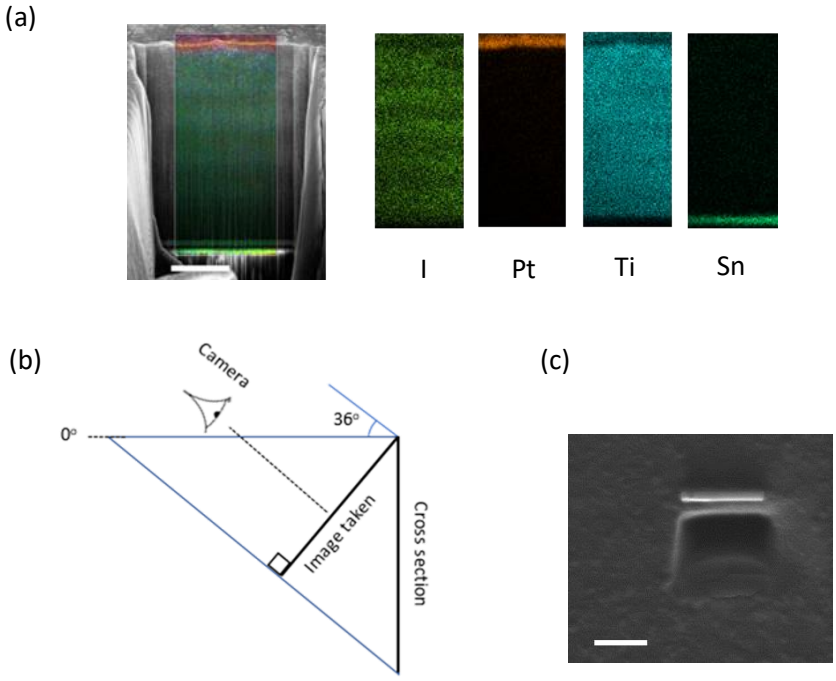

Fig. S12 (a) Cross-section FIB-SEM / EDX image of the anode side of an opened Ply-I DSSC with N719 as absorber. The scale bar is 5 µm, however due to the angle of the camera and image (see Fig. S12 (b)), the actual thickness should be estimated as (the thickness of image taken) / sin(54°) ≈ (the thickness of image taken) × 1.24. The EDX images indicate that the Ply-I is evenly distributed in the mesoporous network from the top surface to the vicinity of FTO. Pt is present on the top of the sample because the sample was marked with Pt for the FIB digging (see Fig. S12 (c)).

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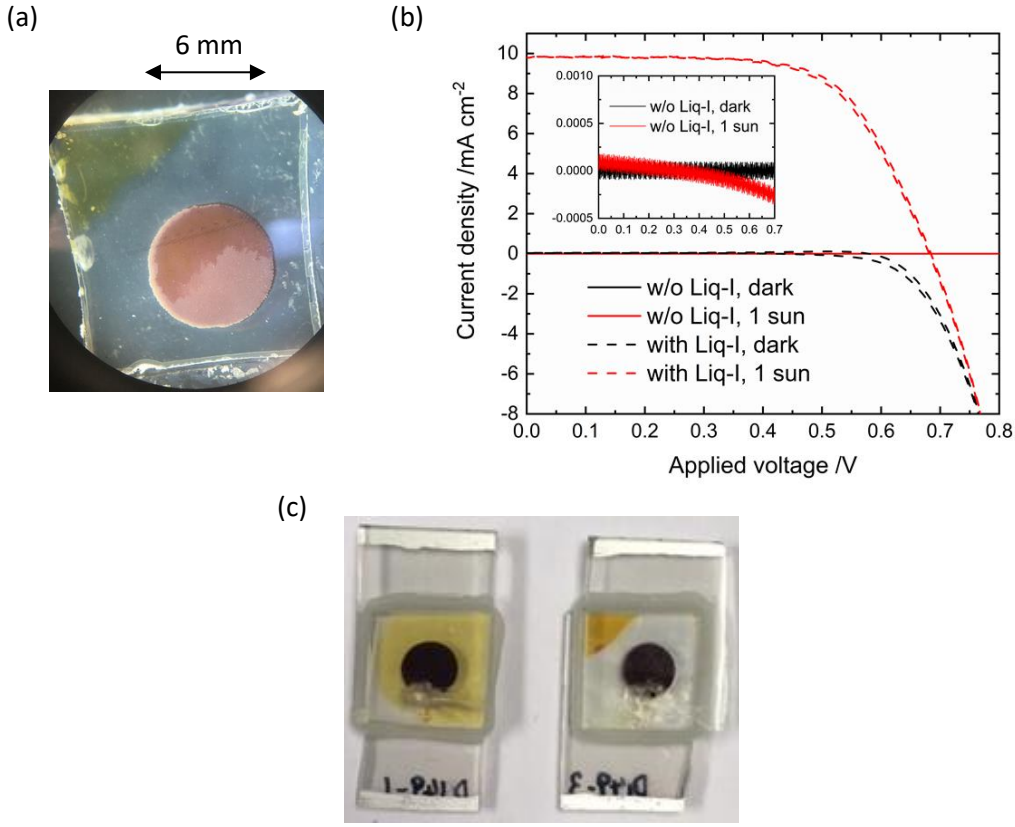

Fig. S13 (a) Optical microscope image of the anode of an opened non-ideal Ply-I DSSC (N719 dye). The diameter of the active area is 6 mm. The dark part on the circle active area is infiltrated/covered with the Ply-I layer (operational) and the pale part has no Ply-I (= no longer operational). Ideally, the whole active area should be dark coloured for optimum performance. The dark yellow part at the corner is the Ply-I formed out of the active area. (b) *J-V* curves of a DSSC with 5T dye before and after injection of the electrolyte (Liq-I), measured in the dark and at 1 sun. The inset shows the very weak current flow of the sample without Liq-I when illuminated at 1 sun. (c) Photographs of a Liq-I DSSC (left) and a Ply-I DSSC (Ply-I) using D149 dye, taken from the cathode side. The Liq-I will fill the entire square area surrounded by the white glue. As it dries, the excess Liq-I outside the active area will be drawn towards the active area (and the corners of the square area). In an ideal case as in Fig. S13 (c), the colour of the active area remains the same (dark all over) as it was in the Liq-I. If the drying has failed, the active area will become paler as seen in Fig. S13 (a). We believe the latter links to the common concept of the electrolyte "drying out".

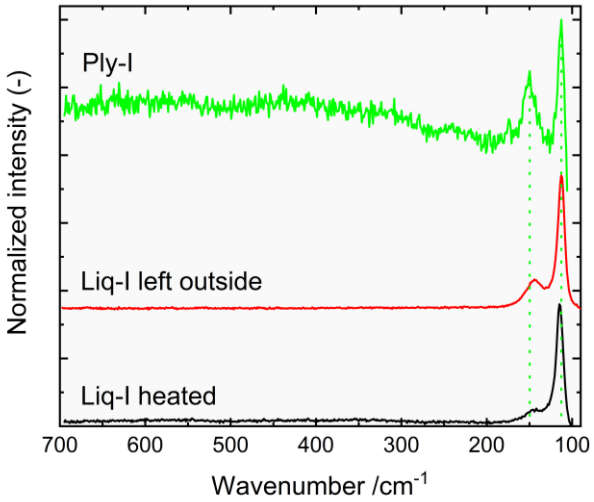

Fig. S14 Raman spectra of the slowly formed Ply-I in the device; Liq-I left outside to dry in ambient air; and Liq-I concentrated by heating at 50 °C. The two peaks in common are situated at 112 cm^{-1} and 143-149 cm^{-1}.

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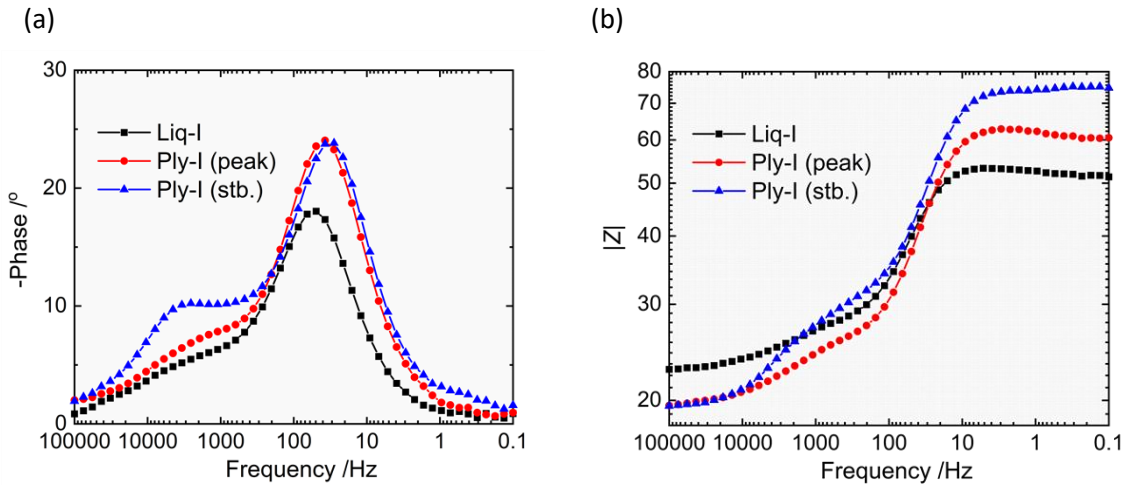

Fig. S15 (a) Bode phase plots of a Liq-I DSSC, Ply-I (peak) DSSC and Ply-I (stb.) DSSC. (b) Bode magnitude plots of the corresponding DSSCs.

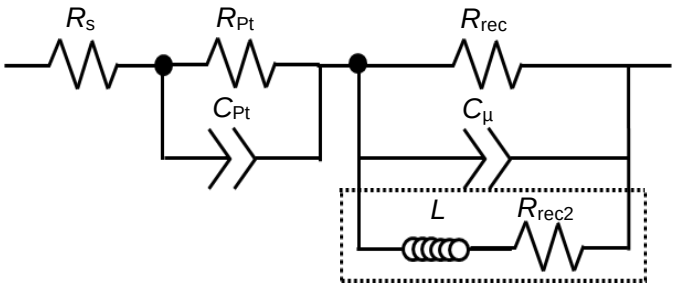

Fig. S16 Proposed equivalent circuit for the electrochemical impedance fitting. R_S: series resistance. R_{Pt}: resistance at the Pt/Ply-I (or Pt/Liq-I) interface. C_{Pt}: capacitance at the Pt/Ply-I (or Pt/Liq-I) interface, derived from a constant phase element. R_{rec}: recombination resistance at TiO_2/Ply-I (or TiO_2/Liq-I) interface. C_μ: chemical capacitance at the TiO_2/Ply-I (or TiO_2/Liq-I) interface, derived from a constant phase element. L: inductance (negative capacitance) at the TiO_2/Pt interface. R_{rec2}: additional recombination resistance at the TiO_2/Pt interface. L_{TiO2} and R_{rec2} were considered in the fitting for the Liq-I DSSC and Ply-I (peak) DSSC.

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