Supporting Information

Polyiodide solid-state dye-sensitized solar cell produced from a standard liquid I\(^{-}/I\(_3^{-}\) electrolyte

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

Dye bath:

N719 dye:\(^[\text{[1]}]\) 0.5 mM N719 in ethanol with 5 mM chenodeoxycholic acid (CDCA). Thickness of the TiO\(_2\) film was \(\sim 20 \mu m\).

D149 dye:\(^[\text{[2]}]\) 0.5 mM D149 in acetonitrile/t-butanol (1:1, v/v) with 1 mM CDCA. The thickness of the TiO\(_2\) film was \(\sim 16 \mu m\).

SQ2 dye:\(^[\text{[3]}]\) 0.3 mM SQ2 in acetonitrile/n-butanol (17:3, v/v) with 3 mM CDCA. The thickness of the TiO\(_2\) film was \(\sim 8 \mu m\).

Spacer:

Surlyn: A 25-\(\mu m\) 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 melted by applying pressure from the top to ensure complete sealing.
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.
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 cm².
Fig. S3 J-V curves of the best Ply-I (stb.) DSSC at the different stages of drying/evolution, measured with a 0.0625 cm² aperture: before drying (Liq-I, t = 0); after 170 h (Ply-I (peak)); after 1500 h (Ply-I (stb.) 1500h) and after 8000 h (Ply-I (stb.) 8000h).

Table S1 Photovoltaic characteristics of the best Ply-I (stb.) DSSC at 0 h (Liq-I), 120 h (Ply-I (peak)), 1500 h and 1800 h (Ply-I (stb.)) using a 0.0625 cm² aperture.

| With 0.0625 cm² | 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     |
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 \ldots $T_{80}$

$T_{S80}$: 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 \ldots $T_{S80}$

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 \ldots $T_{80}$

$T_{S80}$: 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 \ldots $T_{S80}$
Calculation of $\eta_{1000}$ 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) $\eta_{1000}$ 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) $\eta_{1000}$ 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.
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 cm².

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 cm²) 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 cm²) 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.
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/I₃ 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+I₂ and (d) LiI+I₂ placed on filter paper, freshly coated (red) and left for a week (black). The blue triangle indicates the peak overlap with DMPII or LiI.
Table S2 Assignment of the peaks in the IR spectra in Fig. 7.[4*]

| Wavenumber /cm⁻¹ | Symbol       | Vibration mode                                      |
|------------------|--------------|-----------------------------------------------------|
| 3756             | Asterisk     | -OH stretching of H₂O (g)                          |
| 3600-3200        | Filled diamond | -OH stretching of H₂O (l)            |
| 3100-3000        | Open square  | =C-H stretching                                   |
| 2960             | Open triangle | -C-H stretching                                   |
| 2349             | Asterisk     | O=O=C stretching of CO₂ (g)                        |
| 2250             | Filled triangle | -C≡N stretching                        |
| 1720             | Hash         | Unknown peak                                       |
| 1600-1630        | Filled diamond | H-O-H bending of H₂O (l)           |
| 1595             | Asterisk     | H-O-H bending of H₂O (g)                          |
| 1450             | Filled circle | -CH₃ stretching                                   |
| 1380             | Open circle  | -CH₃ bending                                       |
| 1030-1540        | Open diamond  | Unassigned, observed in DMPII+I₂ and Ply-I        |
| 750              | Filled square | -C-H bending                                      |
| 665              | Asterisk     | O=C≡O bending of CO₂ (g)                          |
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)).
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”.

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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.
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. $C_{ui}$: 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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