Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

# ELECTRONIC SUPPLEMENTARY INFORMATION

# A New, Digital Imaging Method to Study Device Lifetime of Multiple Dyes (D35, N719, SQ1 and SQ2) in Dye-sensitized Solar Cells

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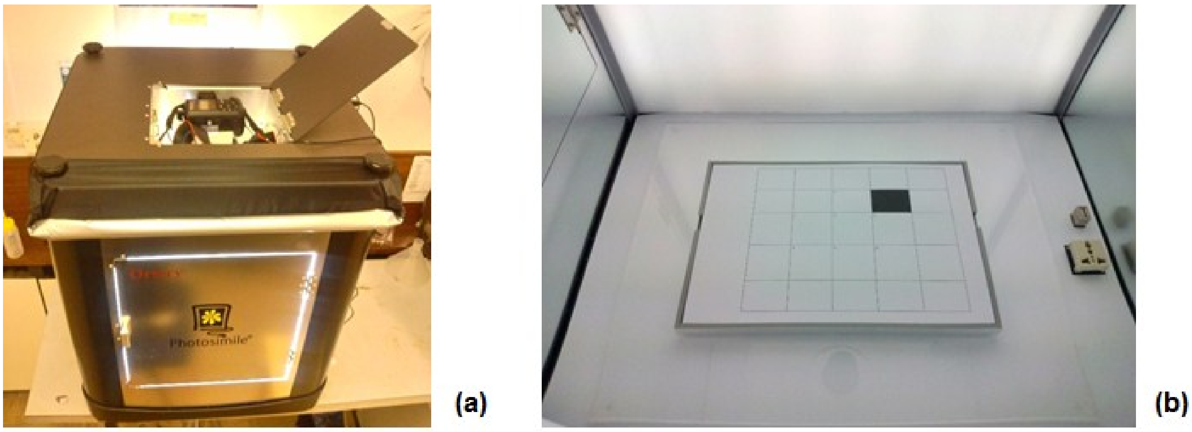
## Light–soaking and digital analysis

A Photosmile 200 lightbox was set up by inserting a Canon EOS 1100D digital camera into the top of the lightbox (ESI Fig. 1a) and connecting the camera to computer using a USB cable. The lights on the lightbox were turned on at least two hours before any testing was started to ensure they had warmed up and the light intensity was stable. Samples for analysis were then placed into the lightbox (ESI Fig. 1b) and the camera was manually focussed. The number and frequency of image capture was then set using DSL Remote Pro and the imaging commenced.

Images were analysed by opening the first image collected using an image editor (e.g. Adobe Photoshop or Microsoft Paint). The coordinates of the four corners of the image were noted and inputted into the macro in Notepad (as highlighted in red in the example macro below). The macro was updated to include the computer directory where the images were saved (highlighted in blue in the example macro below). The file type was changed to BAS by renaming the file from macro.txt to macro.BAS. Sigma Scan was opened and the macro opened and run to analyse the images.

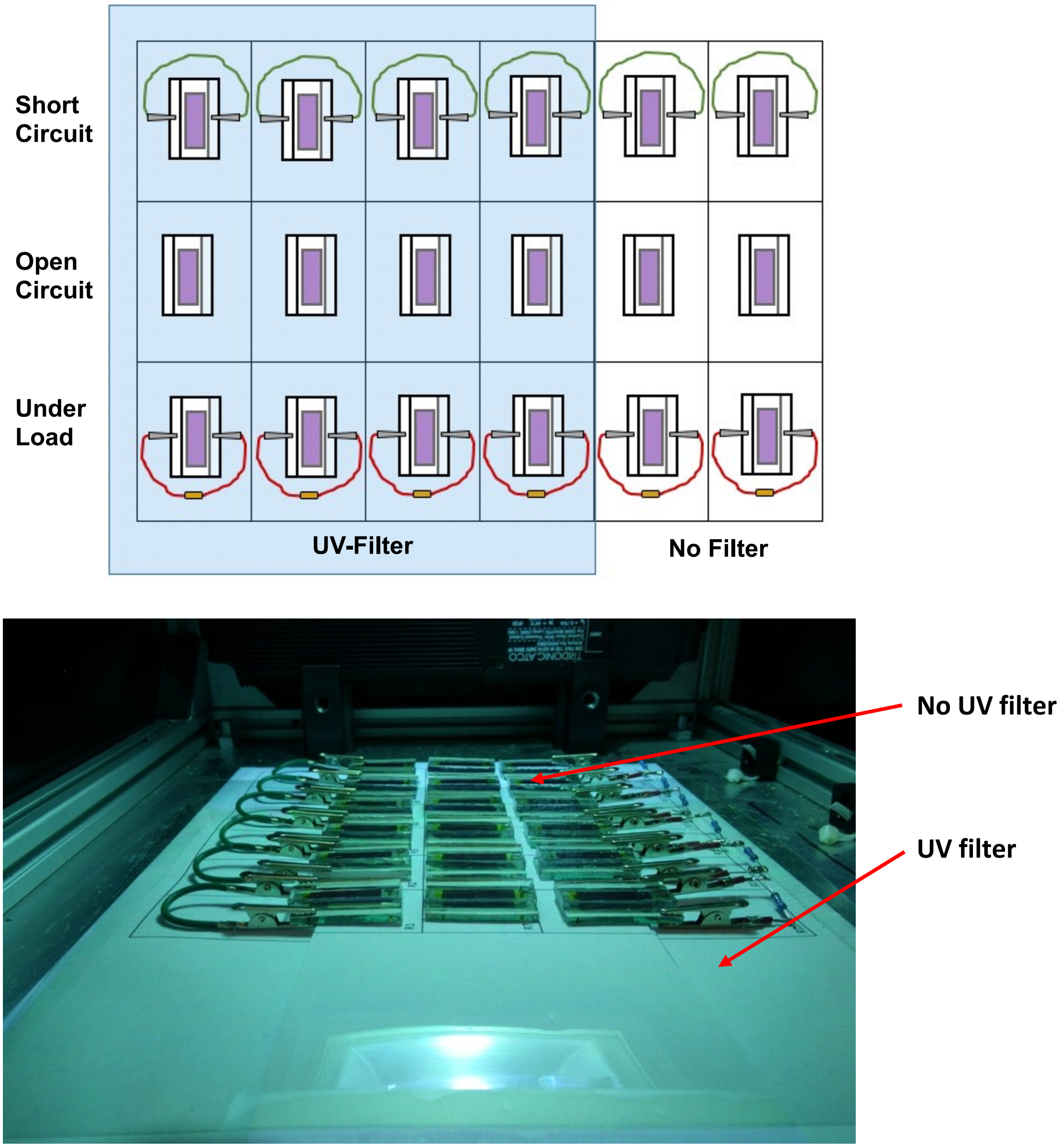


**ESI Fig. 1** (a) Photosmile 2000 lightbox showing Canon digital camera in place above the samples and (b) image of sample grid placed in the lightbox ready for light soaking and analysis.

# ELECTRONIC SUPPLEMENTARY INFORMATION

## Example Macro

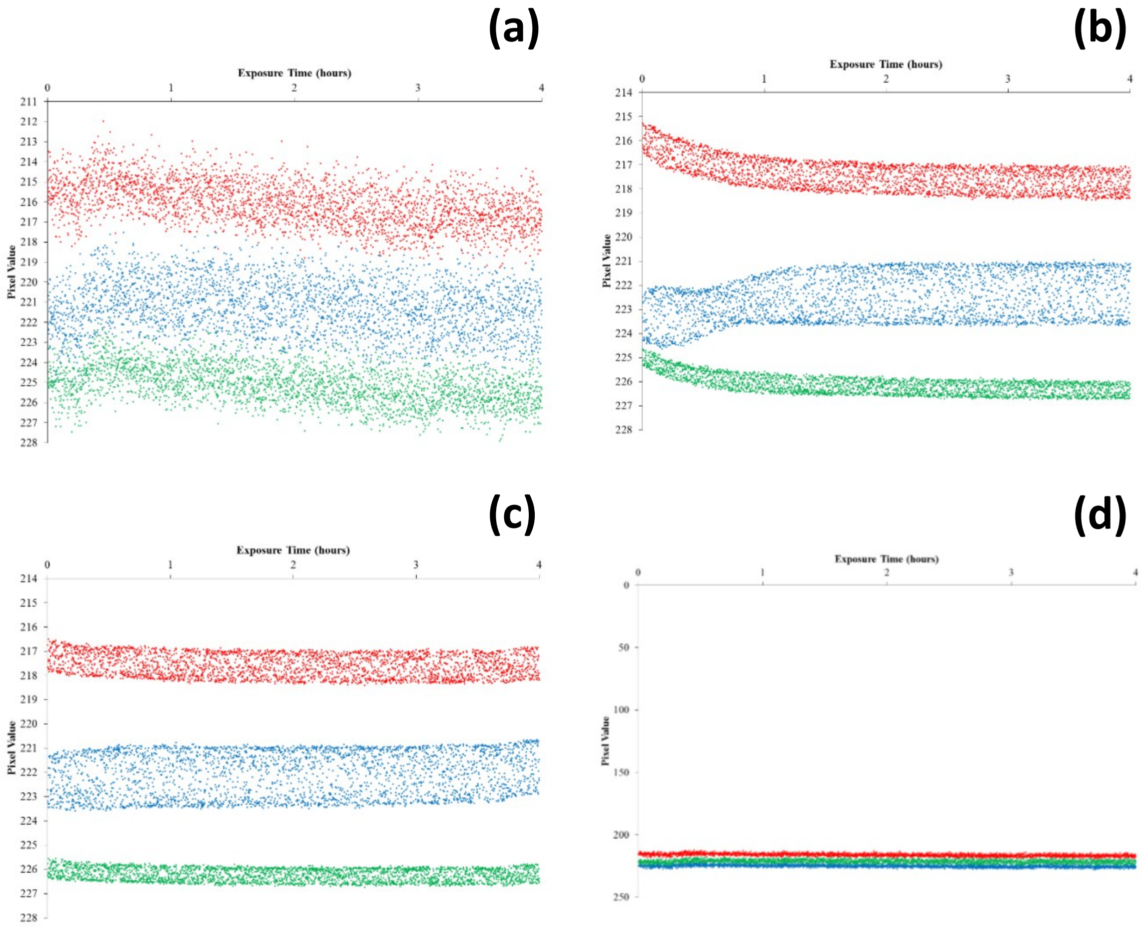
```
Set Worksheet = App.GetWorksheet
For INTN= 0 To 10000
If INTN <10 Then
strpic = "C:\Users\Science\Desktop\Sigma Analysis\IMG_" & "000" & intN & ".jpg"
ElseIf INTN<100 Then
strpic = "C:\Users\Science\Desktop\Sigma Analysis\IMG_" & "00" & intN & ".jpg"
Elseif INTN <1000 Then
strpic = "C:\Users\Science\Desktop\Sigma Analysis\IMG_" & "0" & intN & ".jpg"
Elseif INTN <10000 Then
strpic = "C:\Users\Science\Desktop\Sigma Analysis\IMG_" & intN & ".jpg"
End If
If Dir(strpic) <>"" Then'we have aqn image
Set IMG_0001 = App.OpenImage(strpic)

Worksheet.Show
Worksheet.MakePermanent

ResultCode = IMG_0001.MeasurementLeftClick(1980, 395)
ResultCode = IMG_0001.MeasurementLeftClick(2220, 395)
ResultCode = IMG_0001.MeasurementLeftClick(2220, 635)
ResultCode = IMG_0001.MeasurementLeftClick(1980, 635)
ResultCode = IMG_0001.MeasurementRightClick(1980, 395)

Set IMG_0001=Nothing
End If
Next INTN
'Recorded Macro Ends
End Sub
```



**ESI Fig. 2** (Top) schematic of the DSC device testing experiment (plan view) showing rows of replicate devices either with or without a UV filter. The top row is at short circuit with a wire between the 2 electrodes, the middle row is at open circuit with no connection between the 2 electrodes and the bottom row is under load with a resistor between the 2 electrodes. Bottom image shows the devices ($TiO_2$ active area 0.5 x 2cm) light soaking in the Dyesol UPTS.

## Error analysis for light box

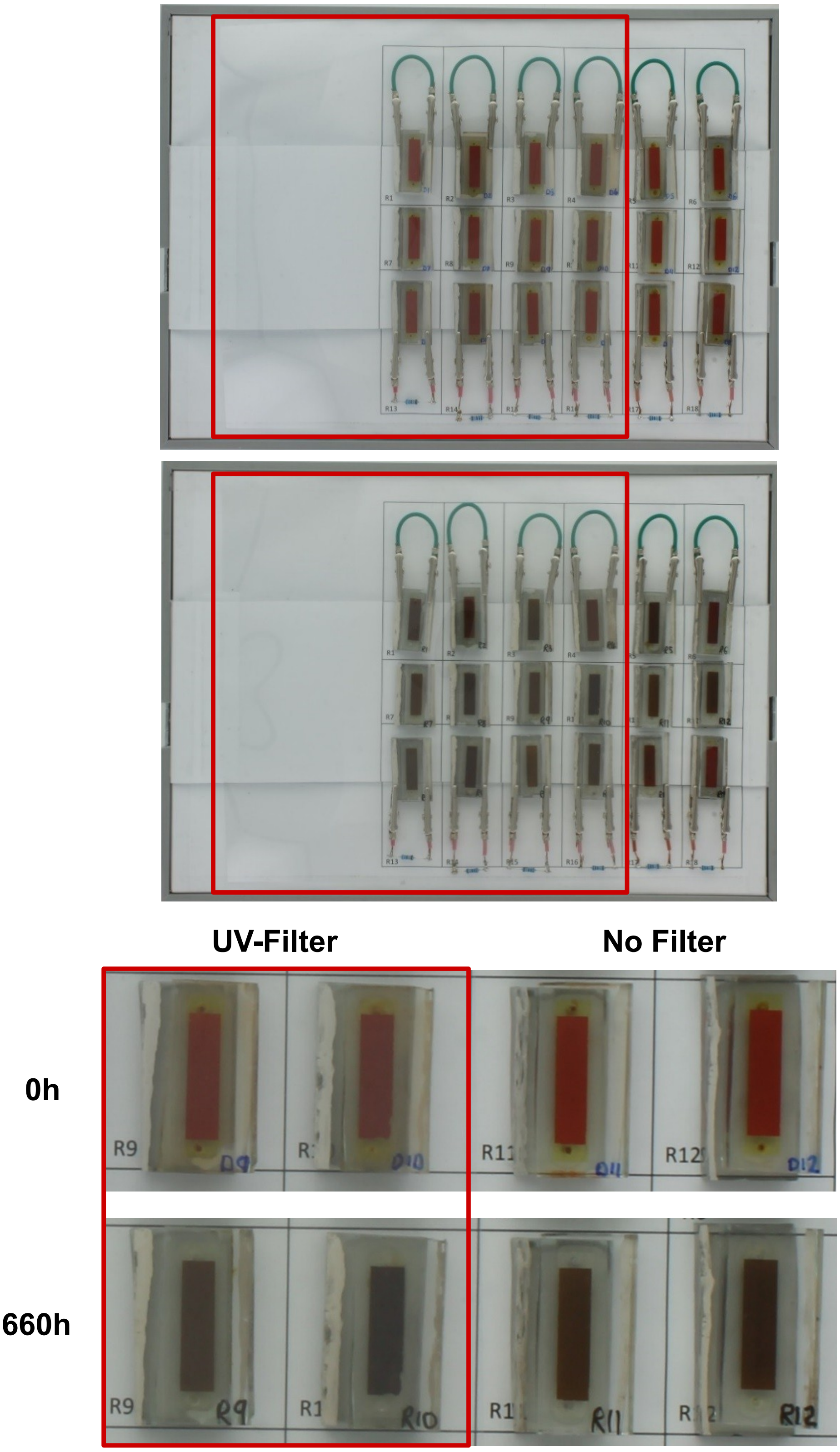
The light intensity in the light box was kept as constant as possible to enable accurate comparison of images between different dyes over time. To enable this, the lens was set to manual and the same white balance, ISO, aperture and shutter speed were used. The light box was also given time to warm up to allow for a consistent intensity at the start of an experiment. ESI Fig. 3 shows the error using an undyed $TiO_2$ control film. Images were taken at 5s intervals and then analysed with Sigma Scan (see ESI Fig. 3).



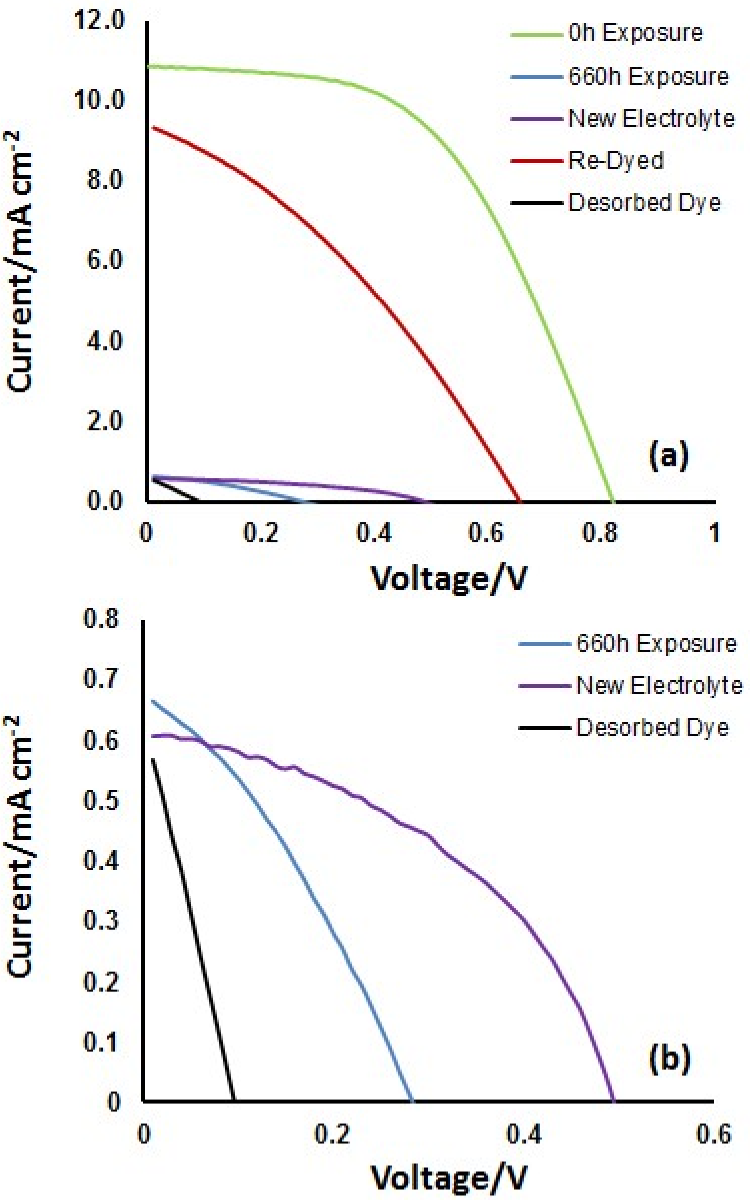
**ESI Fig. 3** RGB pixel intensity data for $TiO_2$ film over 4h light exposure for (a) shutter speed of 0.04s, (b) shutter speed of 0.3s, (c) shutter speed of 0.3s where the light box was switched on 2h before measurements to ensure the lamp stabilization and (d) re-scaled to 0-250 confirming the light intensity remain stable.

**ESI Table 1** The error analysis of each of the methods detailed in ESI Fig. 3, showing a greatly reduced error for (c) and (d) compared with (a).

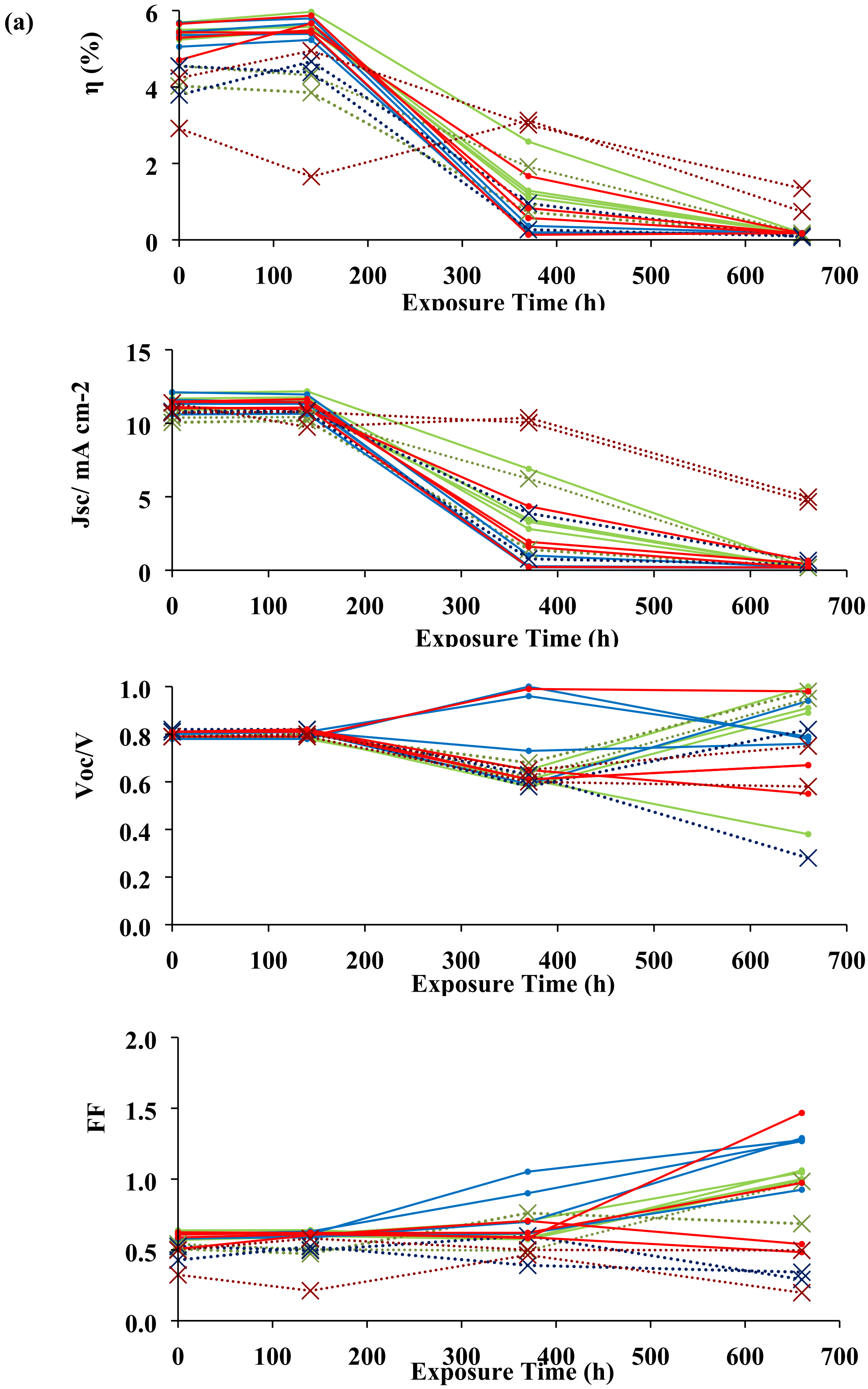
| Method/Stats | Method (a) | | | Method (b) | | | Method (c), (d) | | |
|---|---|---|---|---|---|---|---|---|---|
| Pixel | Red | Green | Blue | Red | Green | Blue | Red | Green | Blue |
| Max | 219.26 | 227.90 | 224.95 | 218.46 | 226.75 | 224.64 | 218.41 | 226.74 | 223.58 |
| Min | 211.98 | 221.49 | 217.22 | 215.28 | 224.65 | 220.95 | 216.51 | 225.55 | 220.65 |
| Range | 7.28 | 6.42 | 7.73 | 3.18 | 2.09 | 3.69 | 1.90 | 1.19 | 2.93 |
| Half Range | 3.64 | 3.21 | 3.87 | 1.59 | 1.05 | 1.85 | 0.95 | 0.59 | 1.46 |
| Standard deviation | 1.09 | 0.97 | 1.31 | 0.62 | 0.39 | 0.91 | 0.45 | 0.26 | 0.88 |
| Standard Error | 0.020 | 0.018 | 0.025 | 0.011 | 0.007 | 0.017 | 0.008 | 0.005 | 0.016 |



**ESI Fig. 4** Digital images of D35-dyed DSC devices (numbered from top left to bottom right from R1 to R21) after (a) 0h light exposure, (b) 370h light exposure and (c) magnified images of UV-filtered and unfiltered devices (R9-R12) showing both the D35 dye and electrolyte colours. Red box denotes the UV filtered samples.

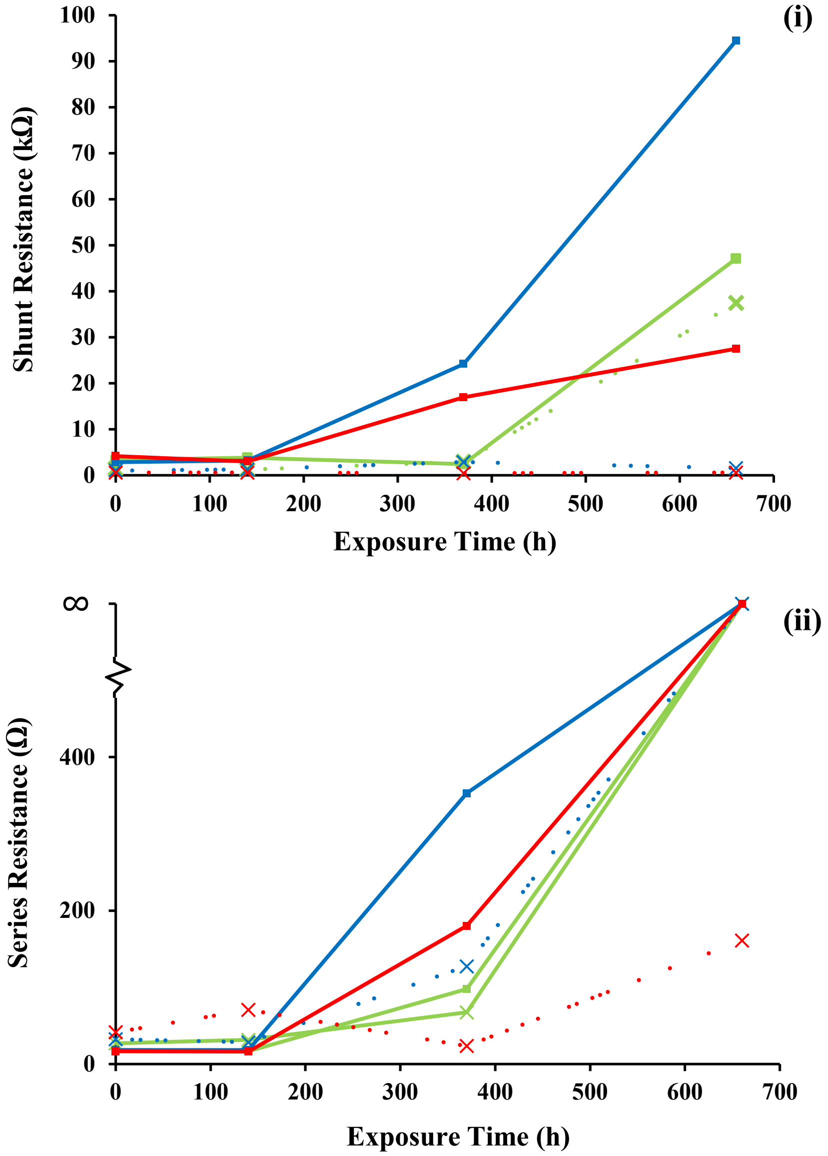


**ESI Fig. 5** IV device data for D35-$TiO_2$ DSC devices (a) at time zero (green line), after 660 h light soaking (blue line), after adding new electrolyte (purple line), after dye desorption using $^{t}Bu_4NOH$ (black line) and then after re-dyeing with D35 (red line) and (b) close-up of selected low efficiency devices for clarity.

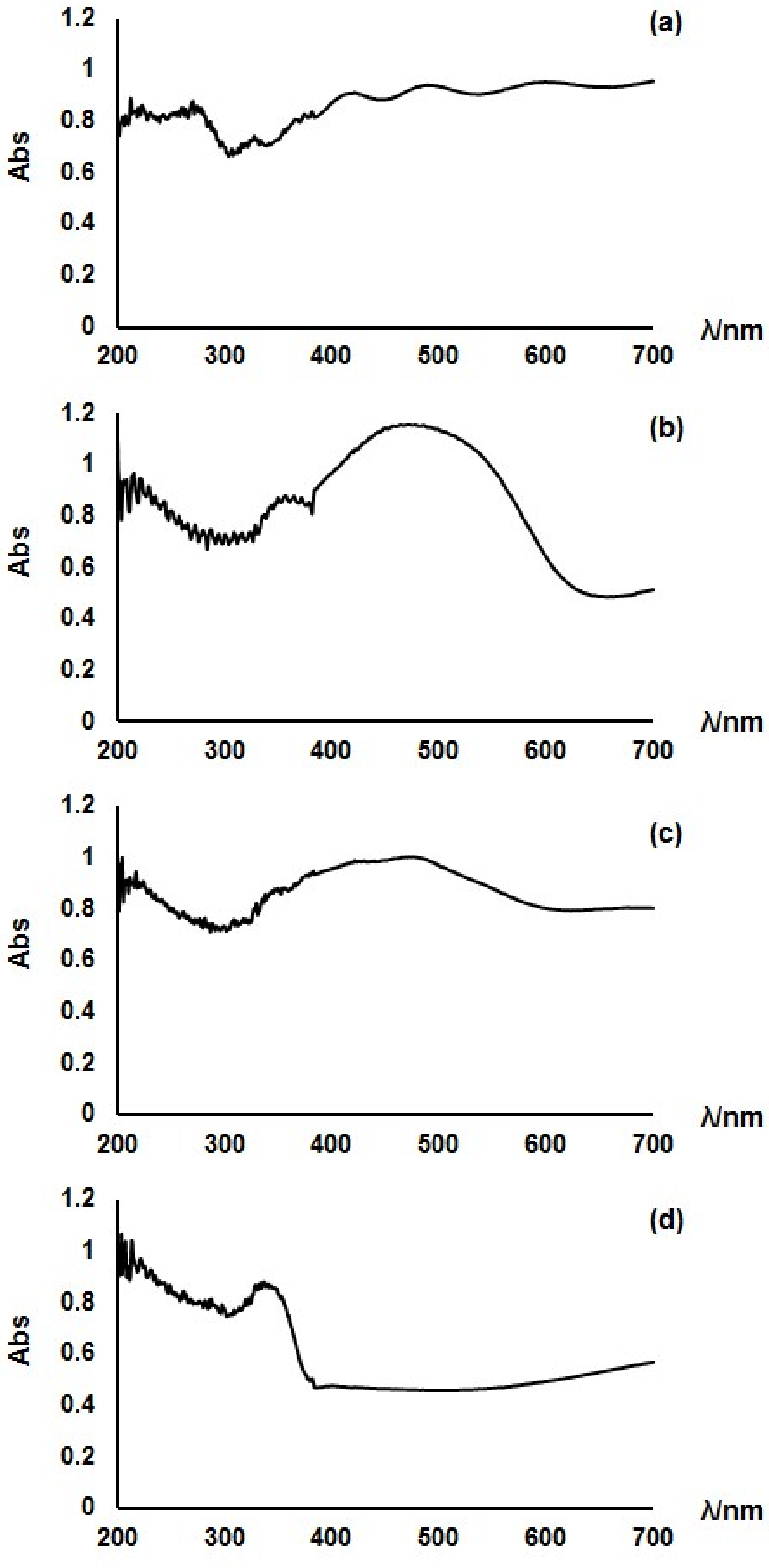


**ESI Fig. 6a** IV data for D35-dyed DSC devices light soaked for 700 h. Open circuit (blue), short circuit (green), under load (red), cSi control (yellow). UV filtered (solid), unfiltered (dotted).

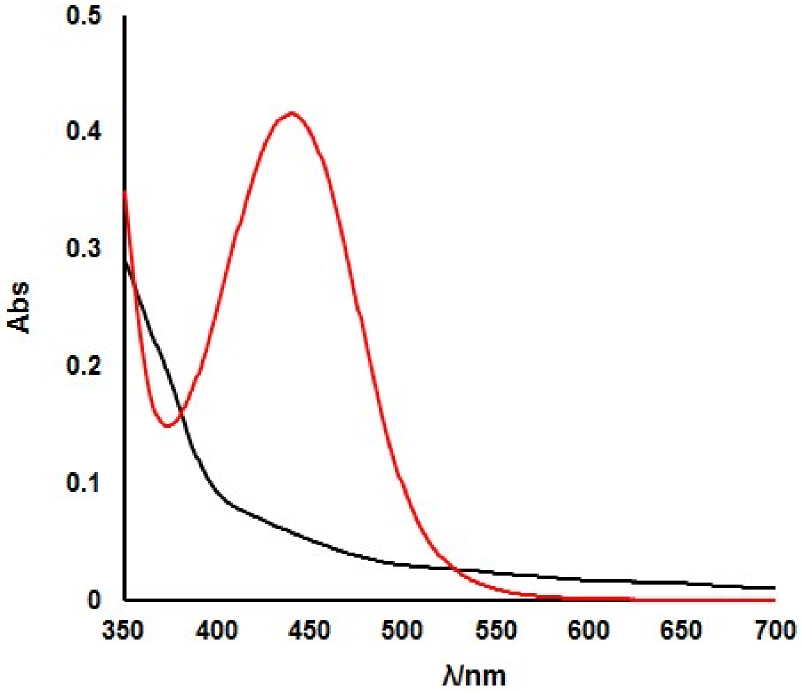
**(b)**



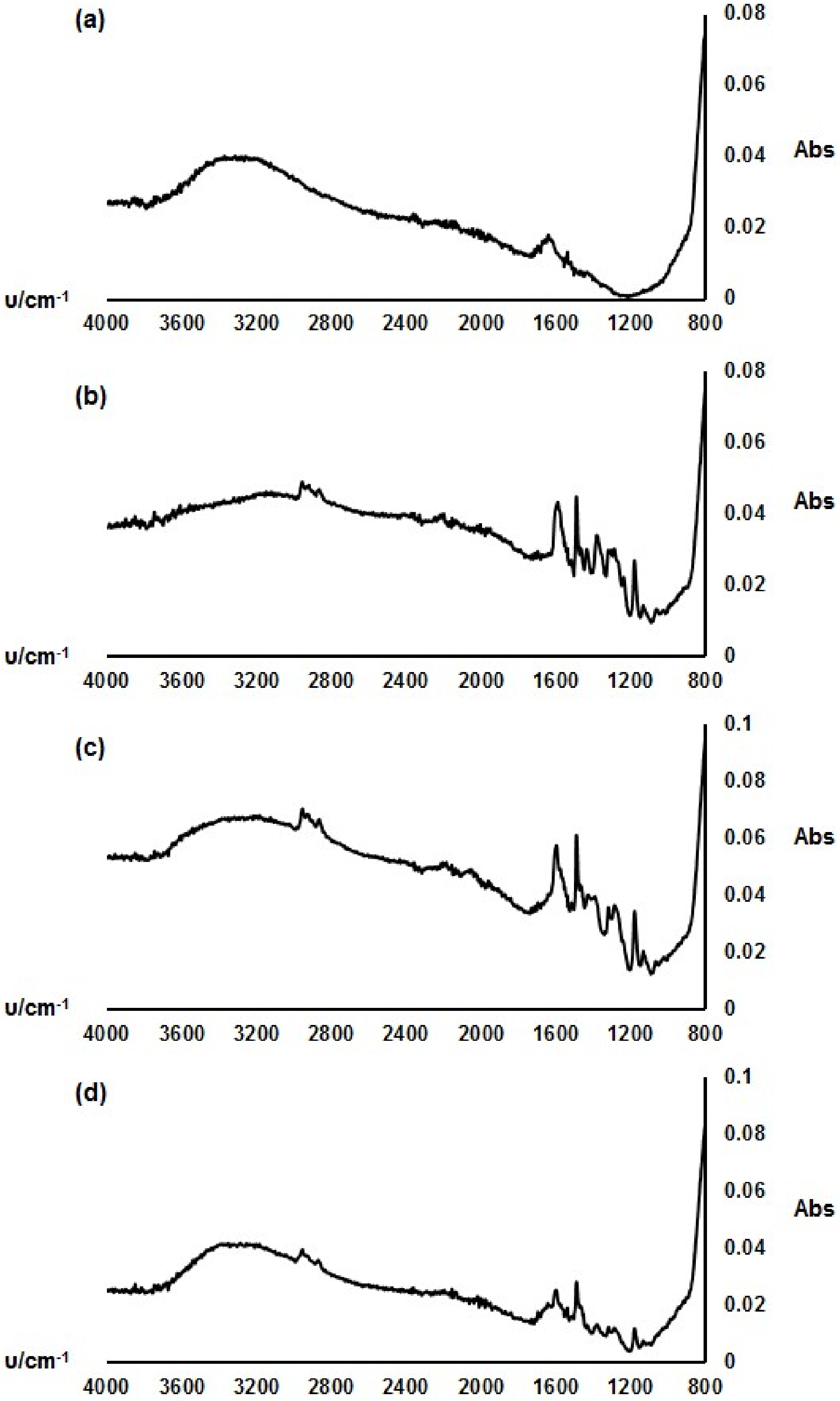
**ESI Fig. 6b** (i) average shunt resistance for D35 DSC devices light-soaked under a Dyesol® UPTS lamp (400Wm$^{-2}$) either with (solid lines & circles) or without (dashed lines & crosses) a UV-filter. Devices were held under a 10Ω load (red lines), open (blue lines) or short circuit (green lines), (ii) average series resistance for the same set of DSC devices.



**ESI Fig. 7** Diffuse reflectance UV-visible spectroscopy of (a) mesoporous $TiO_2$ film, (b) D35 adsorbed onto a mesoporous $TiO_2$ film, (c) a D35-dyed $TiO_2$ film after 660 h light soaking and (d) a light soaked D35-$TiO_2$ film after D35 desorption using ${}^{t}Bu_4NOH_{(aq)}$



**ESI Fig. 8** Solution UV-visible spectra of D35 dye before dyeing (red) and after 660 h light exposure on $TiO_2$ followed by desorption using $^{t}Bu_4NOH_{(aq)}$ (black)



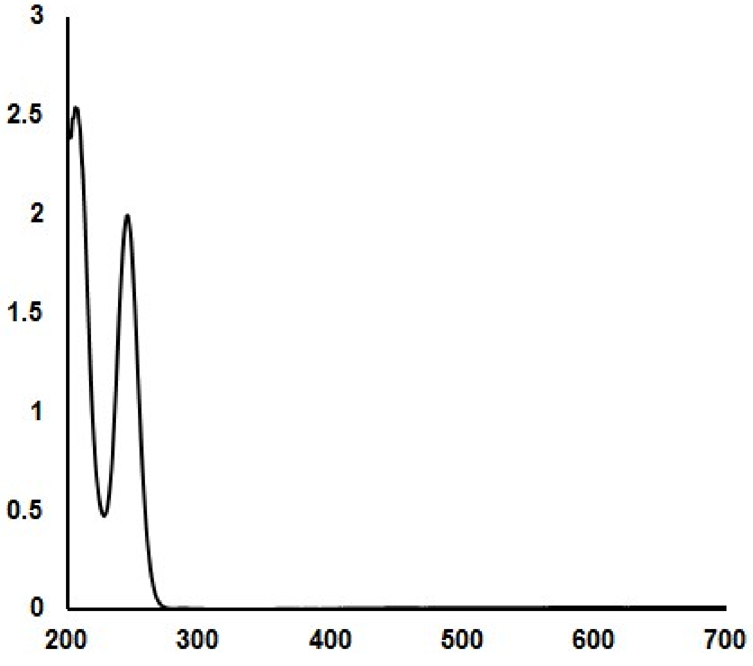
**ESI Fig. 9** ATR infrared spectroscopy of powders of (a) a mesoporous $TiO_2$ film, (b) D35 adsorbed on $TiO_2$, (c) a D35-dyed $TiO_2$ film after 660 h light soaking and (d) a light soaked D35-$TiO_2$ film after D35 desorption using ${}^{t}Bu_4NOH_{(aq)}$

## Electrolyte analysis

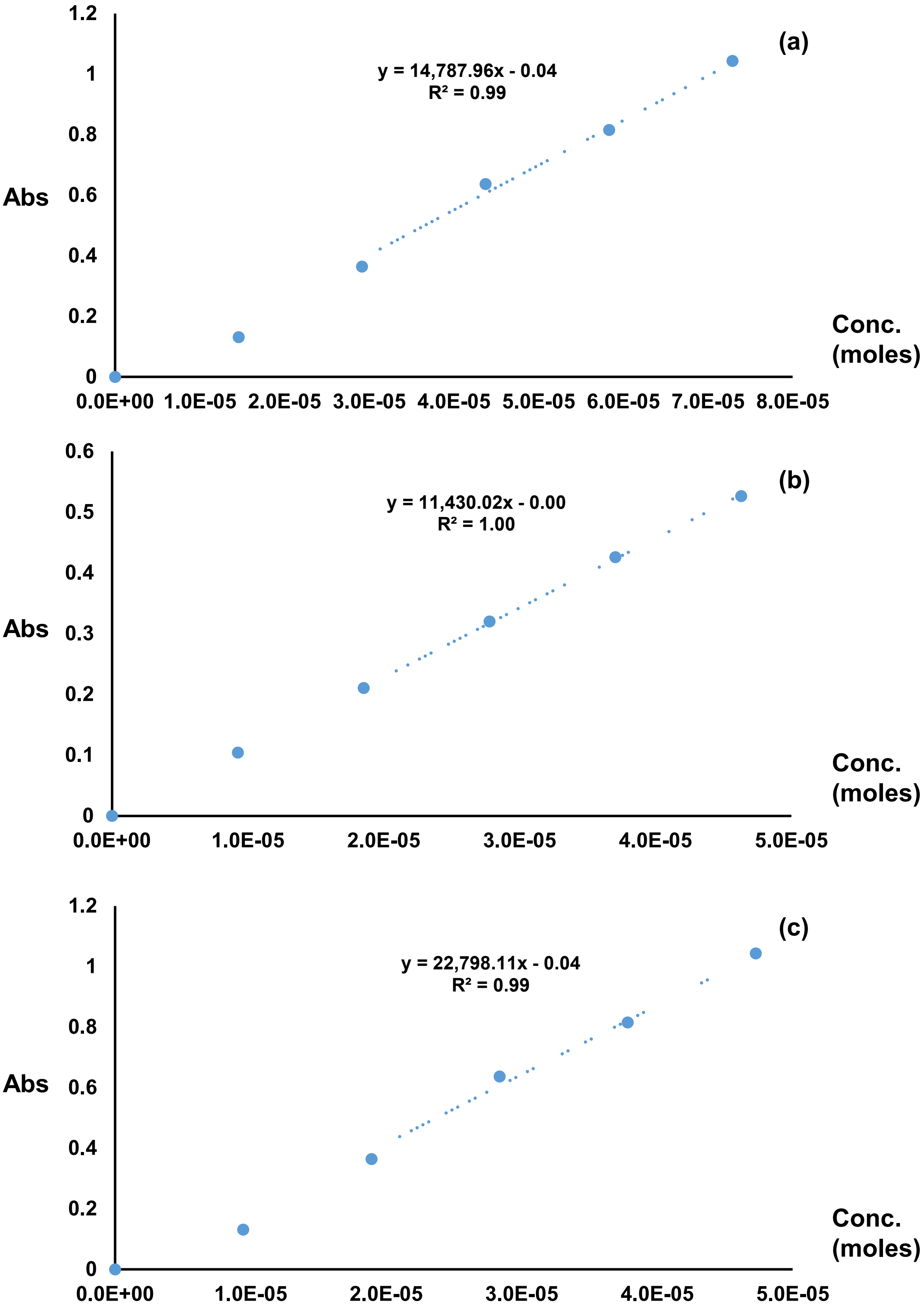
To quantify the iodine and iodide in the electrolyte, firstly the cover slides sealing the drilled holes in the counter electrodes of the DSC devices were removed using a scalpel. Then ten aliquots of 100µl of anhydrous acetonitrile (Sigma-Aldrich) were pumped through the cell using a micropipette. The effluent was collected and the resulting solution was analysed by UV-visible spectroscopy in a 1 mm path-length quartz cuvette. Assuming there was *ca.* 20µl volume of electrolyte inside each device, this corresponds to a 50-fold dilution.

The UV-visible spectrometer was calibrated for iodide at 245 nm using LiI (ESI Fig. 10 and 11a) and iodine at 363 nm (ESI Fig. 11b). A further calibration was carried out (ESI Fig. 11c) using by mixing equal concentrations of LiI and $I_2$ to produce tri-iodide ion ($I_3^-$) which, along with $I^-$, is one of the key redox ions found in the DSC electrolyte. The $\lambda_{max}$ for $I_3^-$ was also 363 nm. Acetonitrile was used as the solvent again to mimic the solvent used in the DSC devices.

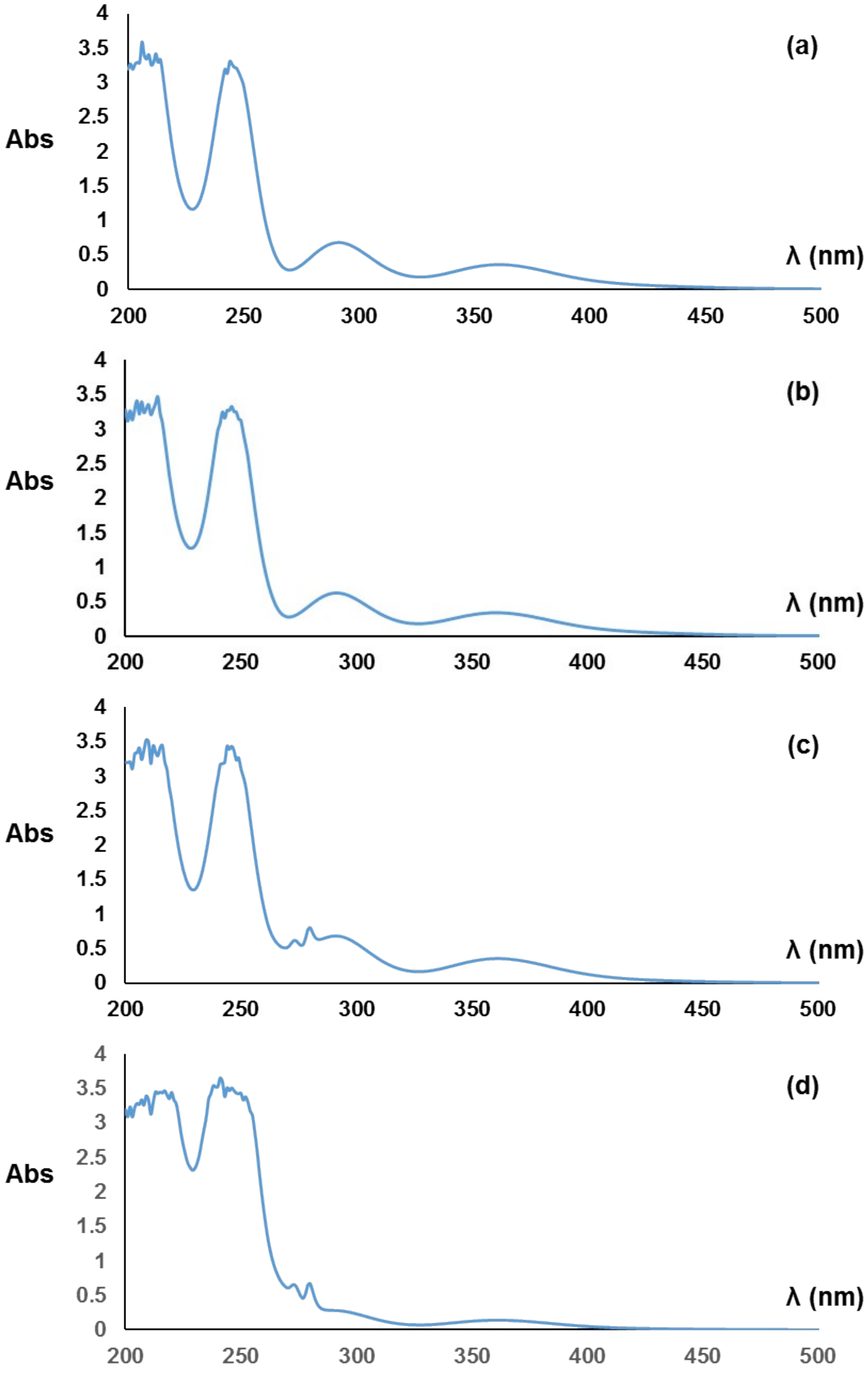
The data show that, after 2500 h of light soaking without UV filtering, the N719 device electrolyte contains 20.7 mM $I_3^-$. By comparison, the UV filtered, light soaked N719 electrolyte contains 52.5 mM $I_3^-$ (ESI Fig. 12c and d). By comparison, after 660 h of light soaking, the UV filtered D35 electrolyte contains 53.0mM $I_3^-$ whilst the unfiltered D35 electrolyte contains 42.5 mM $I_3^-$ (ESI Fig. 27a and b). These compare to an initial 50mM $I_2$ in both the N719 and D35 electrolytes. Thus, these data confirm that, for the N719 devices, the $I_2$ (and associated $I_3^-$) are degraded before the dye over 2500 h of light soaking. Conversely, because the D35 devices degrade over a period of *ca.* 350 h with or without UV irradiation, the $I_2$ and associated $I_3^-$ are still present at close to their initial concentrations and so are not limiting device performance.



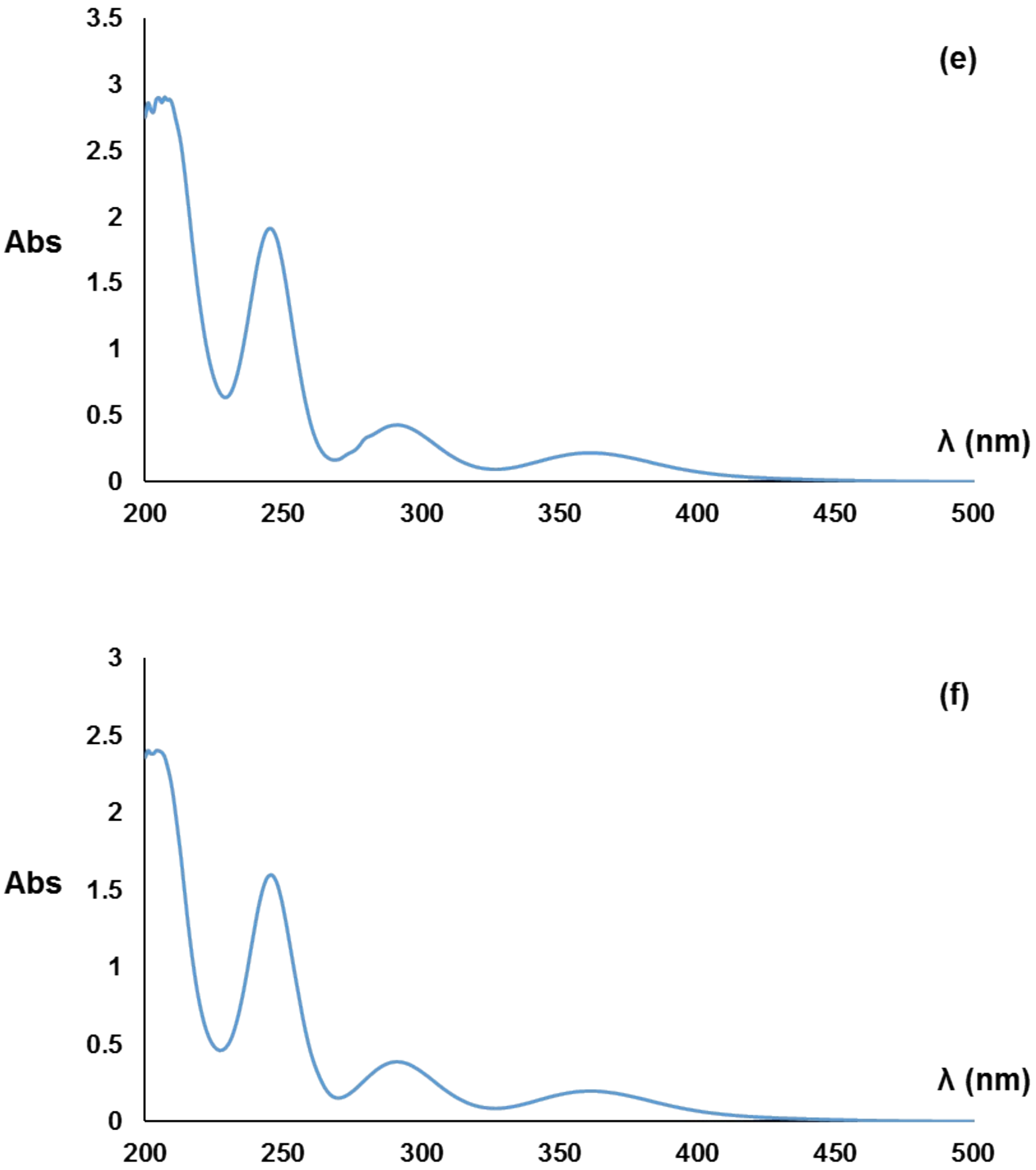
**ESI Fig. 10** Example of solution UV-visible spectrum of LiI in acetonitrile



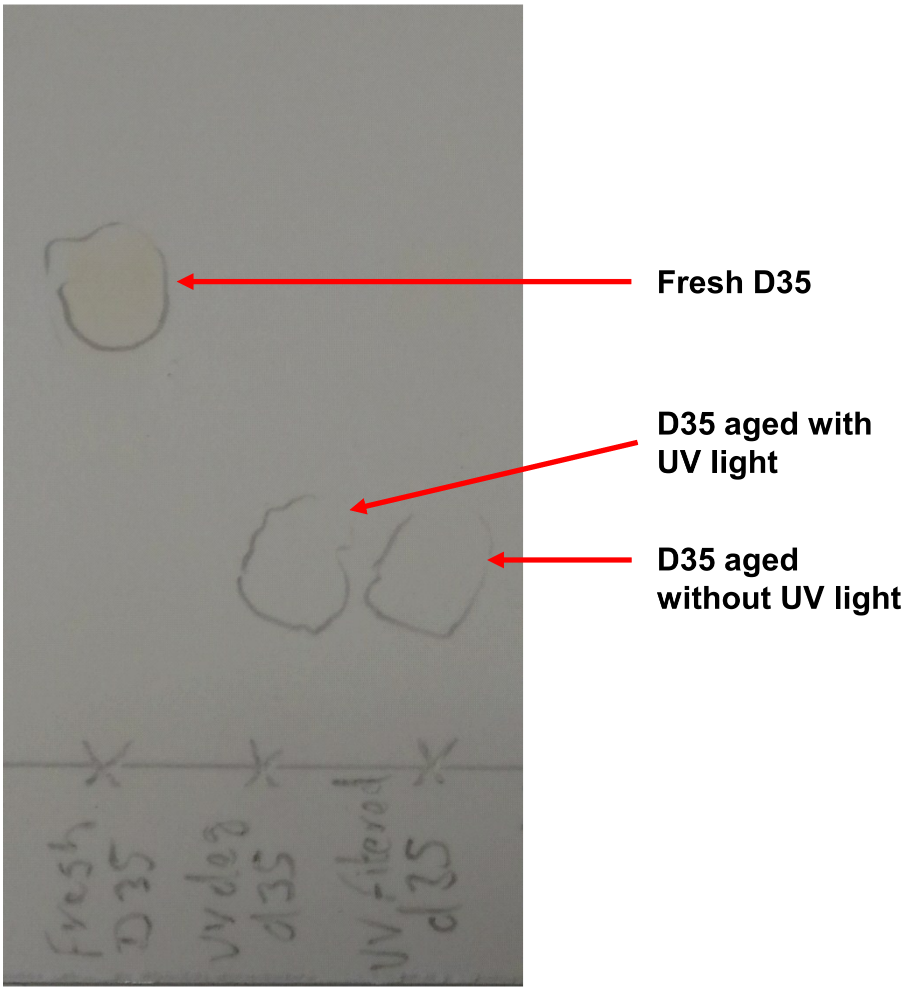
**ESI Fig. 11** Calibration data for UV-visible spectroscopy of (a) LiI for $\lambda_{max}$ = 245 nm, (b) $I_2$ for $\lambda_{max}$ = 363 nm and (c) equimolar mixtures of LiI and $I_2$ for $\lambda_{max}$ = 363 nm. Solvent is anhydrous acetonitrile.



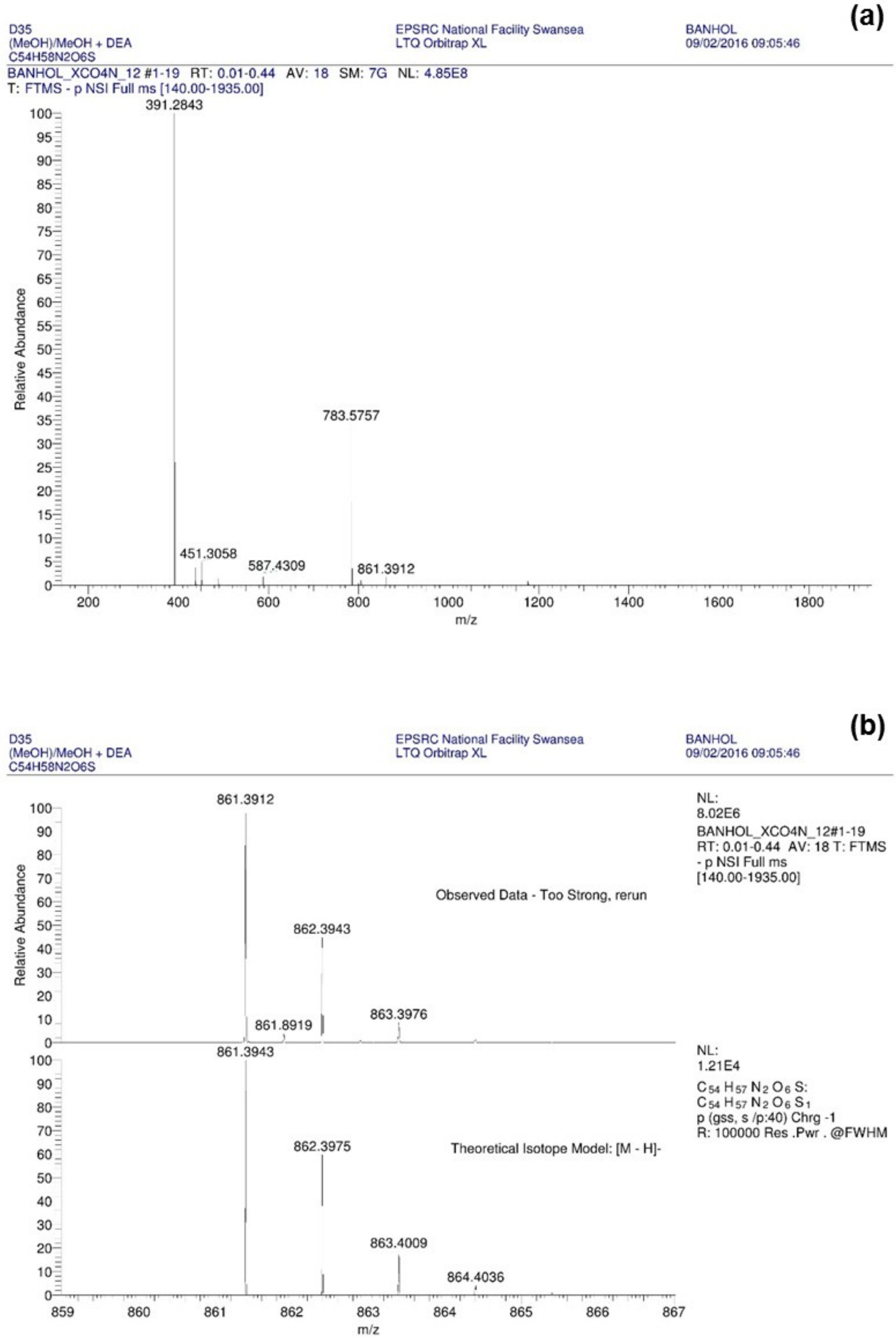
**ESI Fig. 12** UV-visible spectroscopy of D35 electrolyte aged for 660 h (a) with UV filtering and (b) without UV filtering and also N719 electrolyte aged for 2500 h (c) with UV-filtering and (d) without UV filtering. Solvent in all cases is anhydrous acetonitrile.



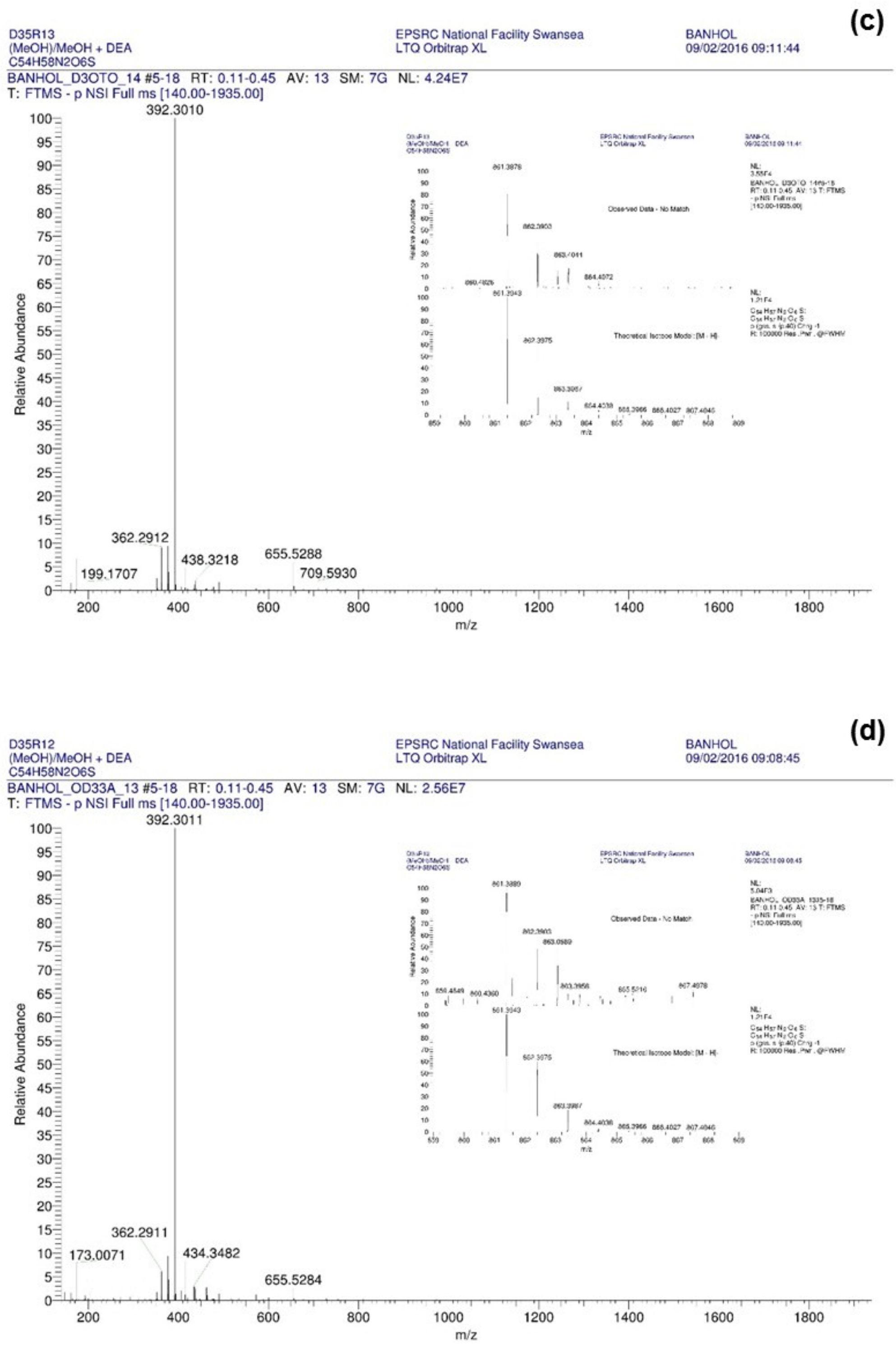
**ESI Fig. 12 cont.** UV-visible spectroscopy of (e) unaged D35 electrolyte and (b) unaged N719 electrolyte. Solvent is anhydrous acetonitrile.



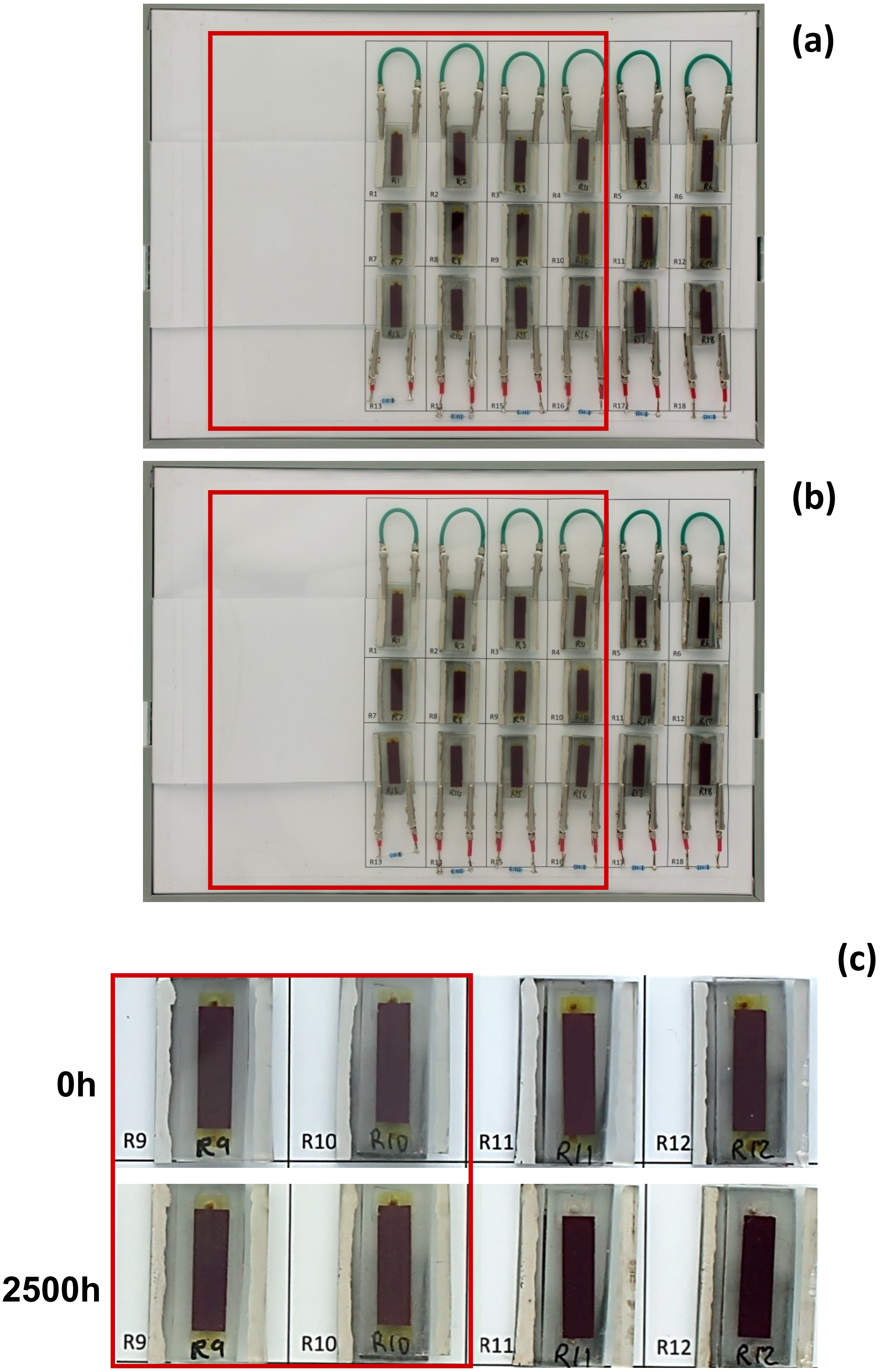
**ESI Fig. 13** Thin layer chromatography of neat D35 dye (left), and D35 dye aged for 660h either without UV filtering (middle) or with UV filtering (right). The significant shift in the D35 $R_f$ value after ageing shows that the D35 is changed by exposure in devices. The similar $R_f$ values for UV filtered and unfiltered D35 samples show that the dye ages in the same way regardless of the presence of UV light.



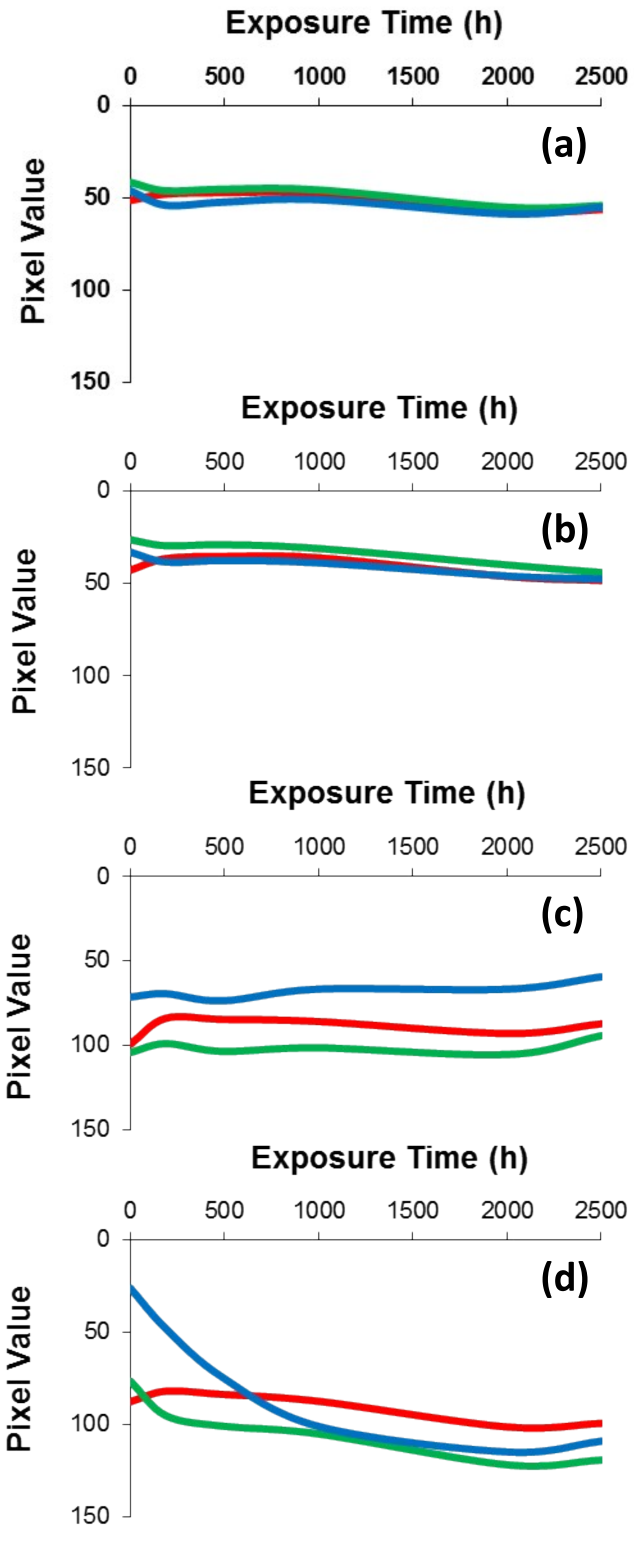
**ESI Fig. 14** Negative ion mass spectrum of pristine D35 run by electrospray injection (ESI) on LTQ Orbitrap XL 1 (a) shows mass range from 140 to 1935 a.m.u. and (b) shows isotope pattern and accurate mass for D35 molecular ion [M-H]$^-$.



**ESI Fig. 14 cont.** Negative ion ESI mass spectra of D35 dye desorbed from 660h light soaked photo-anodes showing (c) UV filtered sample and (d) sample without UV filtering. Main figures show mass range from 140 to 1935 a.m.u. and inserts shows isotope pattern and accurate mass for D35 molecular ion [M-H]$^-$.

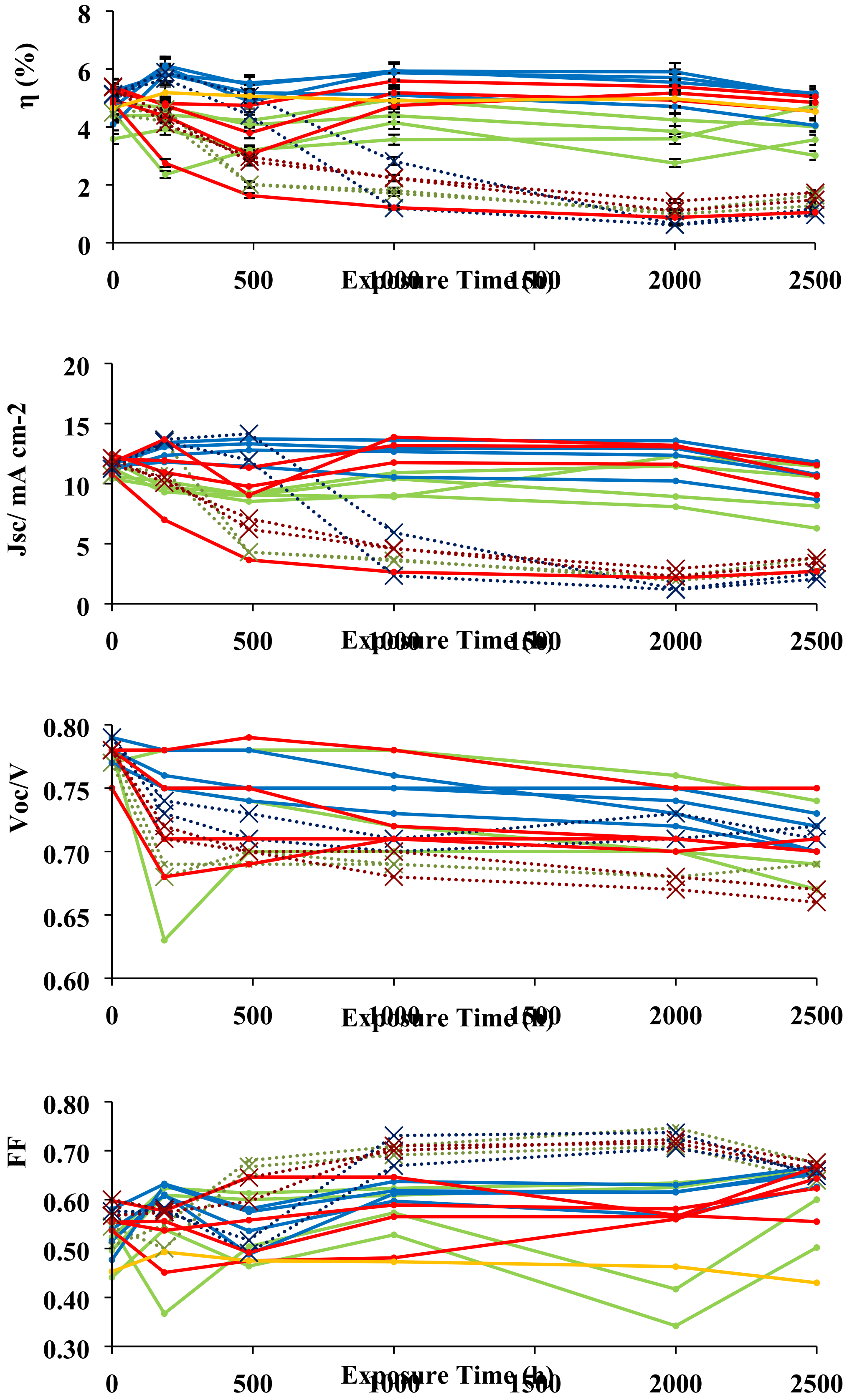


**ESI Fig. 15** Digital images of N719-dyed DSC devices (numbered from top left to bottom right from R1 to R21) after (a) 0h light exposure, (b) 2500h light exposure and (c) magnified images of UV-filtered and unfiltered devices (R9 – R12) showing both the N719 dye and electrolyte colours. Red box denotes the UV filtered samples.



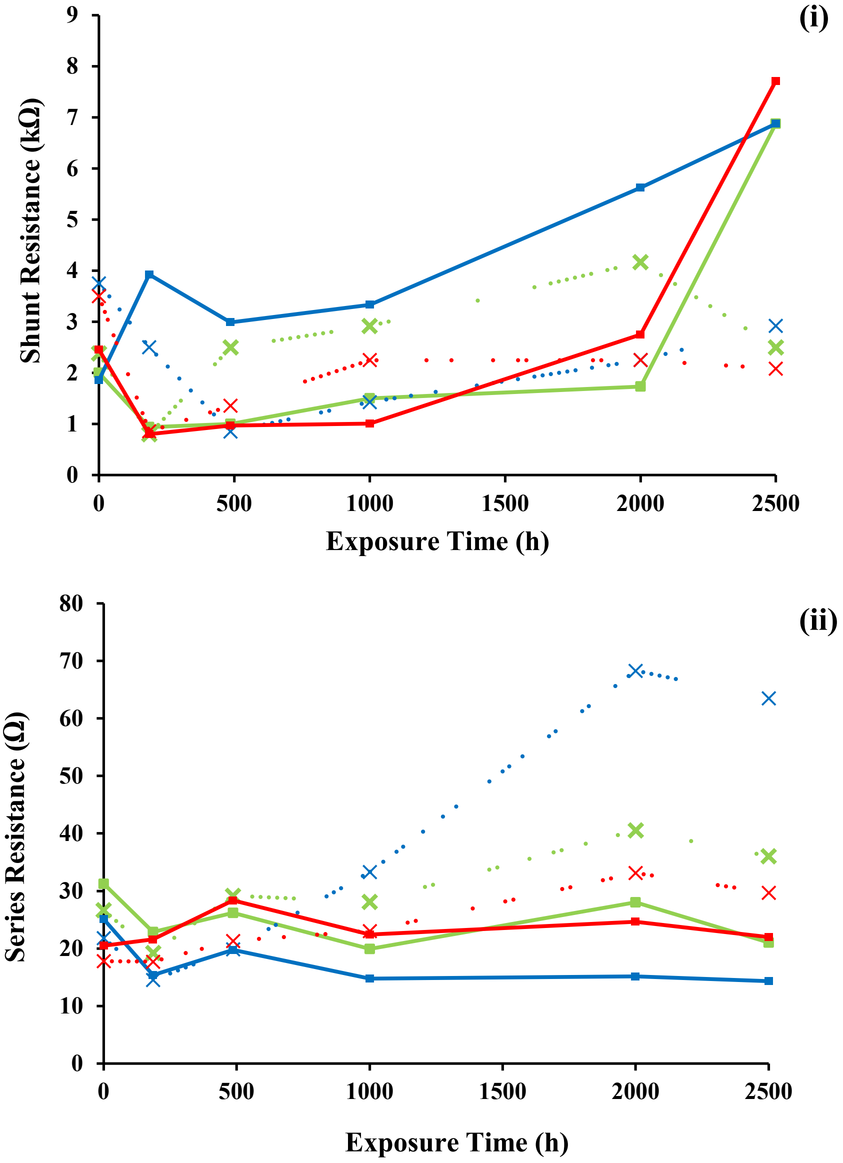
**ESI Fig. 16** RGB pixel intensity data for N719 DSC devices light soaked for 2500h. The data show examples of the RGB data for dyed $TiO_2$ photo-electrode films which were (a) UV-filtered and (b) unfiltered. Areas of devices which showed only electrolyte were also analysed and examples of data for (c) UV-filtered and (d) unfiltered electrolyte are shown.

(a)

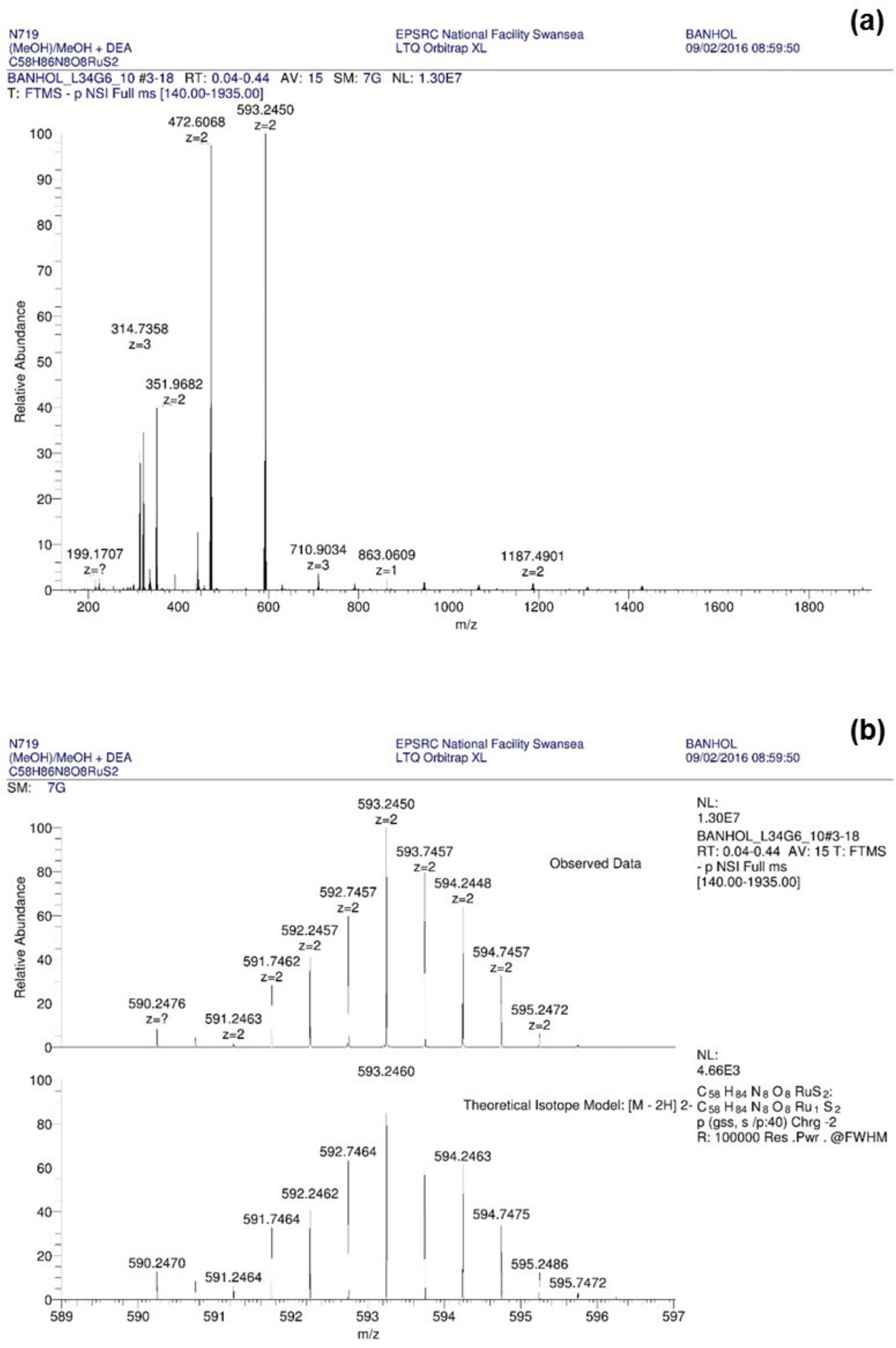


**ESI Fig. 17a** IV parameters for N719-dyed DSC devices light soaked for 2500 h. Open circuit (blue), short circuit (green), under load (red), cSi control (yellow). UV filtered (solid), unfiltered (dotted).

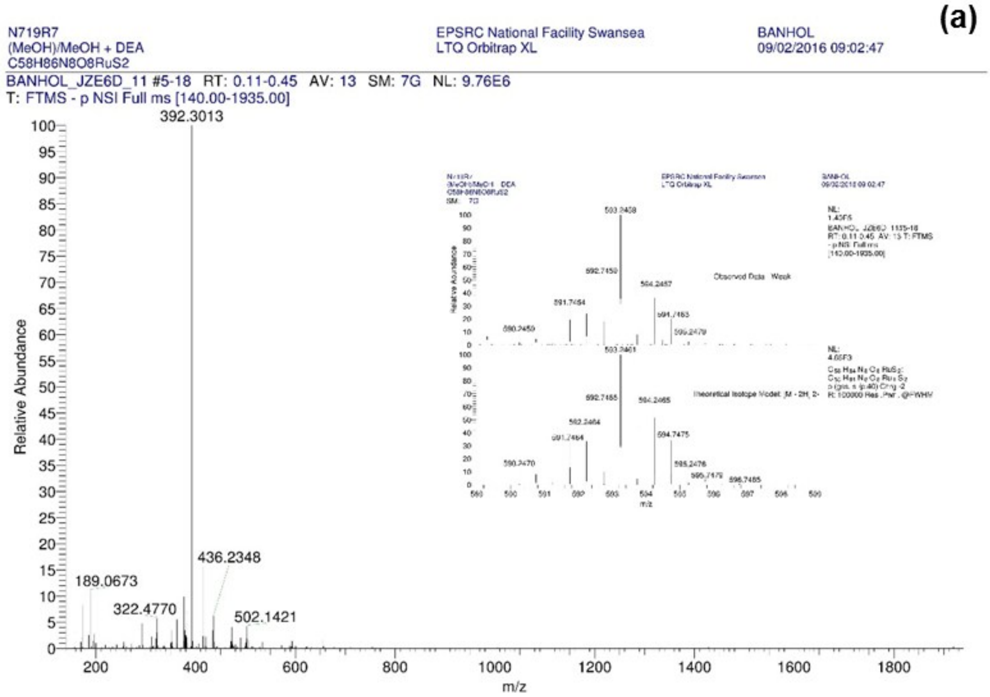
**(b)**

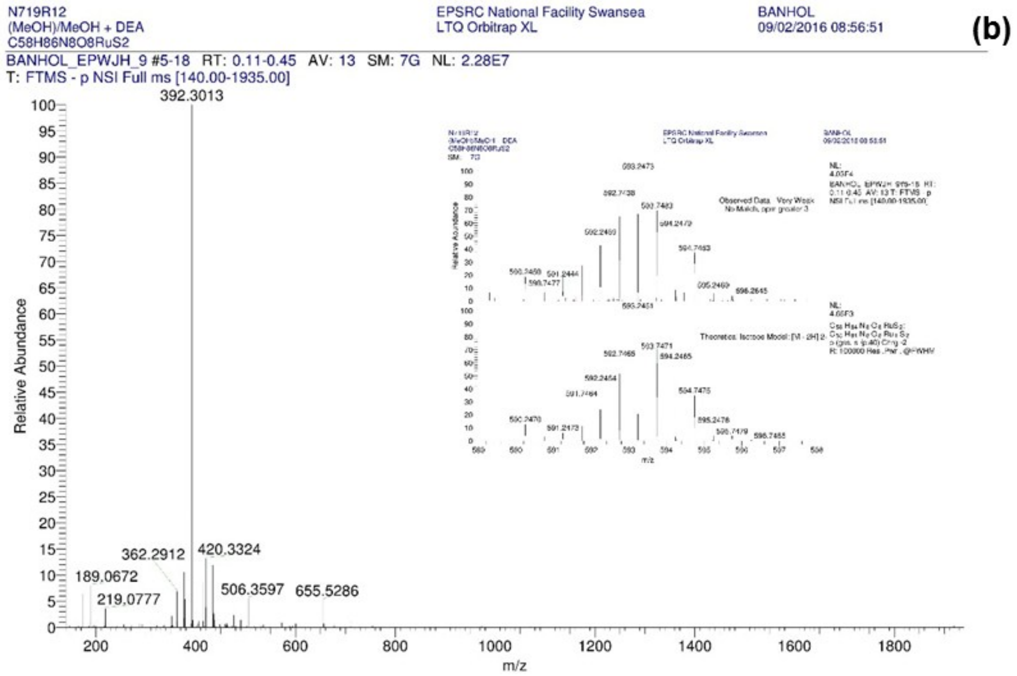


**ESI Fig. 17b** (i) average shunt resistance for N719 DSC devices light-soaked under a Dyesol® UPTS lamp (400Wm$^{-2}$) either with (solid lines & circles) or without (dashed lines & crosses) a UV-filter. Devices were held under a 10Ω load (red lines), open (blue lines) or short circuit (green lines), (ii) average series resistance for the same set of DSC devices.

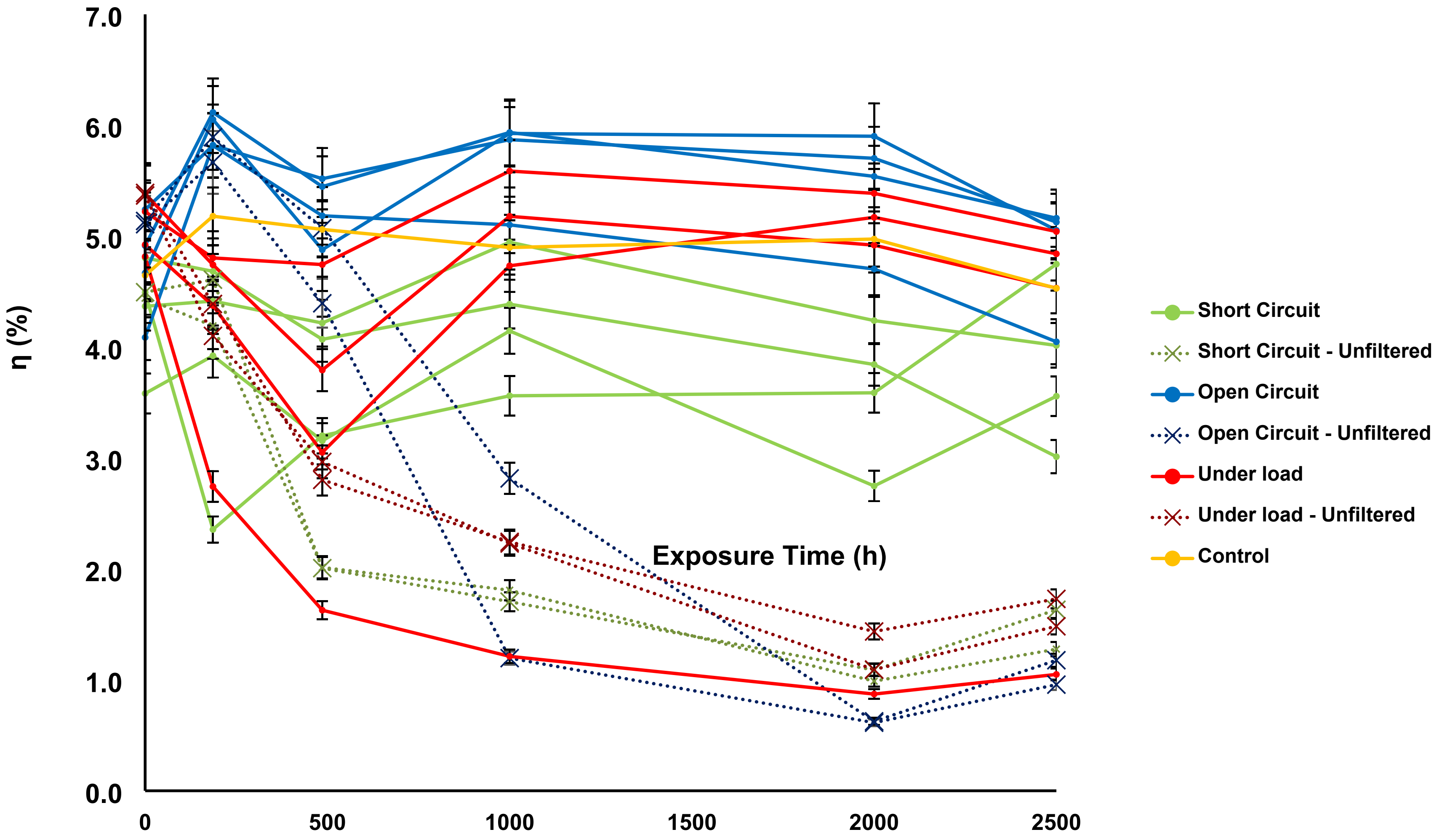


**ESI Fig. 18** Negative ion ESI mass spectrum of N719 run on LTQ Orbitrap XL 1. (a) shows mass range from 140 to 1935 a.m.u. and (b) shows isotope pattern and accurate mass for N719 molecular ion where z = 2, $[M-2H]^{2-}$.

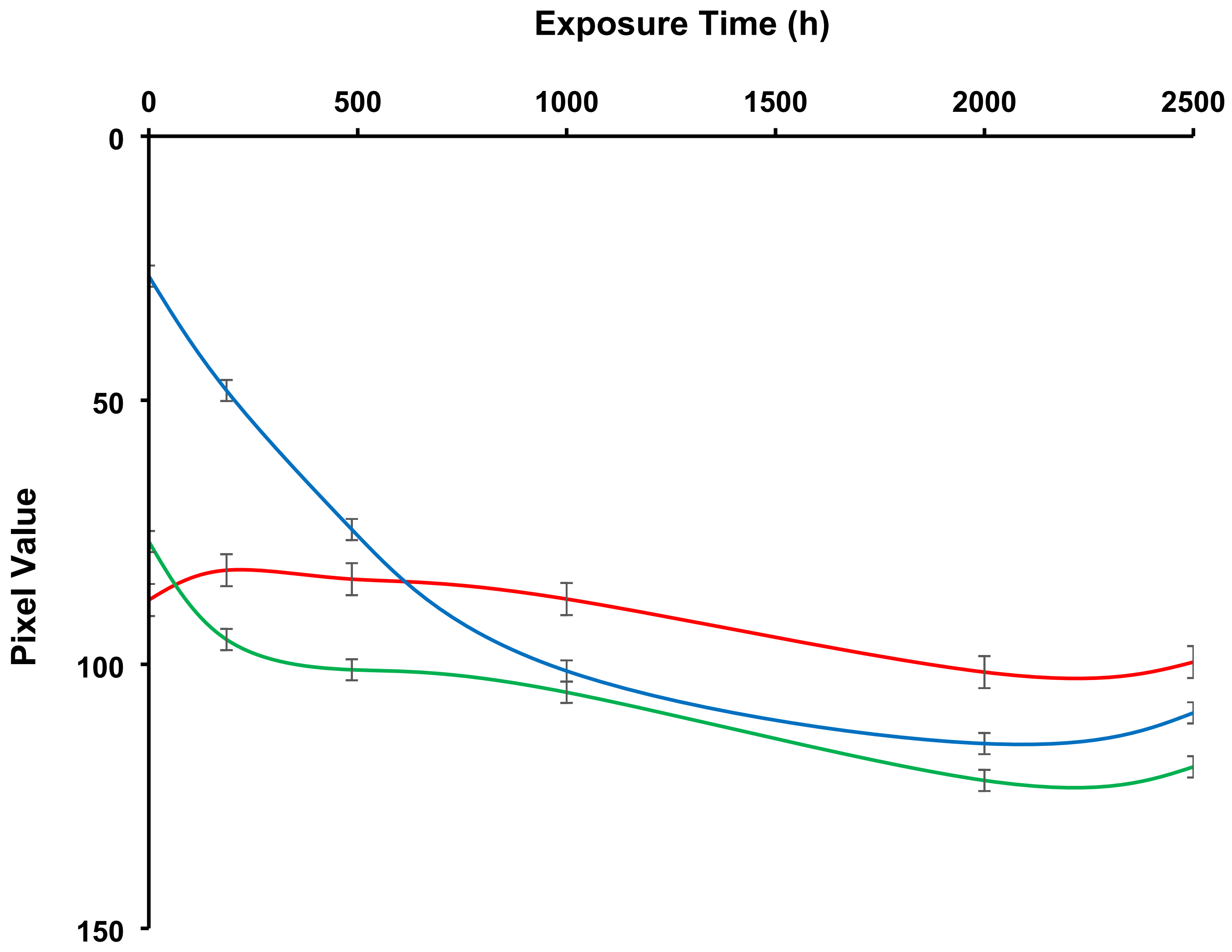




**ESI Fig. 18 cont.** Negative ion ESI mass spectra of N719 dye desorbed from photo-anodes after 2500h light soaking showing (a) UV filtered sample and (b) sample without UV filtering. Main figures show mass range from 140 to 1935 a.m.u. and inserts shows isotope pattern and accurate mass for N719 molecular ion where z =2, $[M-2H]^{2-}$.



**ESI Fig. 19** Efficiency *vs* time for N719-dyed DSC devices light-soaked under a Dyesol® UPTS lamp (400 W $m^{-2}$) either with (solid lines & circles) or without (dashed lines & crosses) a UV-filter. Devices were held under load (red lines) or at open (blue lines) or short circuit (green lines). Error bars shown on all data.



**ESI Fig. 20** RGB pixel intensity data *vs* time for electrolyte colour in N719 DSC devices light-soaked under a Dyesol® UPTS lamp (400 W m$^{-2}$) without a UV filter. Data as shown in Fig. 8b of the paper. Error bars are shown here for clarity.

**ESI Table 2** DSC device data for D35 dyed devices at time zero and after 660 h of light soaking. † The calculation of fill factors after 660 h of light soaking is inconsistent (it should always be < 1.00). This is due to very low $J_{sc}$ and $V_{oc}$ data of the degraded devices and the calculations of the IV software.

| **Initial Measurements** | | | | | **After 660 h light soaking** | | | |
|---|---|---|---|---|---|---|---|---|
| **Device** | **FF** | **η/%** | **$V_{oc}$** | **$I_{sc}$/cm$^2$** | **FF†** | **η/%** | **$V_{oc}$** | **$I_{sc}$/cm$^2$** |
| ***Short Circuit – UV filtered*** | | | | | | | | |
| D1 | 0.58 | 5.7 | 0.81 | 12.06 | 0.99 | 0.2 | 1.00 | 0.18 |
| D2 | 0.64 | 5.5 | 0.79 | 10.90 | 1.06 | 0.2 | 0.89 | 0.18 |
| D3 | 0.57 | 5.4 | 0.81 | 11.68 | 2.64 | 0.2 | 0.38 | 0.18 |
| D4 | 0.58 | 5.2 | 0.79 | 11.50 | 1.05 | 0.2 | 0.91 | 0.18 |
| ***Short Circuit – non UV filtered*** | | | | | | | | |
| D5 | 0.54 | 4.5 | 0.81 | 10.38 | 0.98 | 0.2 | 0.95 | 0.18 |
| D6 | 0.51 | 4.0 | 0.79 | 10.06 | 0.69 | 0.1 | 0.98 | 0.18 |
| ***Open Circuit – UV filtered*** | | | | | | | | |
| D7 | 0.58 | 5.7 | 0.81 | 12.11 | 0.93 | 0.2 | 0.94 | 0.20 |
| D8 | 0.59 | 5.4 | 0.80 | 11.60 | 1.28 | 0.2 | 0.79 | 0.17 |
| D9 | 0.58 | 5.4 | 0.81 | 11.32 | 1.29 | 0.2 | 0.76 | 0.18 |
| D10 | 0.61 | 5.1 | 0.78 | 10.60 | 1.27 | 0.2 | 0.78 | 0.18 |
| ***Open Circuit – non UV filtered*** | | | | | | | | |
| D11 | 0.53 | 4.5 | 0.81 | 10.70 | 0.29 | 0.1 | 0.82 | 0.40 |
| D12 | 0.43 | 3.8 | 0.82 | 10.80 | 0.34 | 0.1 | 0.28 | 0.67 |
| ***Under load – UV filtered*** | | | | | | | | |
| D13 | 0.61 | 5.7 | 0.81 | 11.47 | 1.47 | 0.2 | 0.67 | 0.17 |
| D14 | 0.62 | 5.4 | 0.79 | 11.02 | 0.97 | 0.2 | 0.98 | 0.19 |
| D15 | 0.59 | 5.3 | 0.81 | 11.10 | 0.48 | 0.2 | 0.55 | 0.64 |
| D16 | 0.51 | 4.7 | 0.81 | 11.45 | 0.54 | 0.2 | 0.67 | 0.44 |
| ***Under load – non UV filtered*** | | | | | | | | |
| D17 | 0.50 | 4.2 | 0.79 | 10.73 | 0.50 | 1.3 | 0.58 | 4.66 |
| D18 | 0.32 | 2.9 | 0.79 | 11.39 | 0.20 | 0.7 | 0.75 | 4.97 |

**ESI Table 3** X-ray photoelectron spectroscopic data for ethanol washed (R8) and dye desorbed (R9) D35 devices showing key peaks. *No error available for high resolution data but corresponding wide scans show these data to be representative of the surface.

**$TiO_2$ working electrodes**

| Peak | Approx. Position (eV) | Composition (at%) | | | | Comment |
|---|---|---|---|---|---|---|
| | | R8 | Error | R9 | Error | |
| I 3d | 618.2 | | | 0.14 | 0.05 | FWHM suggests one chemistry, consistent with $I^-$ |
| O 1s | 529.3 | 45.41 | 1.02 | 51.95 | 1.06 | Two chemistries consistent with $TiO_2$ & organic O |
| Ti 2p | 458.3 | 20.13 | 0.58 | 22.85 | 0.77 | Position consistent with $TiO_2$ |
| N 1s | 399.5 (R8)<br>402.0 (R9) | 0.58 | 0.12 | 0.53 | 0.12 | 399.5eV is consistent with surface adsorbed *tert*-butylpyridine<br>402eV is a very high binding energy for organic N. Possibly $R_4N^+$ type species |
| C 1s | 284.8 | 33.88 | 1.35 | 23.83 | 1.67 | Both R8 & R9 show mainly C-C, with some C-O and COOx |

**Pt counter electrodes**

| Peak | Approx. Position (eV) | Composition (at%) | | | | Comment |
|---|---|---|---|---|---|---|
| | | R8 | Error | R9 | Error | |
| I 3d | 618.2 | 0.36 | * | 0.43 | 0.4 | Quite broad, but probably $I^-$ |
| O 1s | 532.0 | 35.8 | * | 27.5 | 6.16 | Two O peaks with highly variable intensities; 532.1 eV is organic C-O, 530.5 eV is $SnO_2$ |
| Sn 3d | 486.5 | 15.7 | * | 6.64 | 2.84 | Consistent with $SnO_2$ |
| N 1s | 401.8 | 2.85 | * | 3.44 | 0.6 | Two N species. Dominant peak at 399.57 eV with a lower intensity 402.04 eV peak ($R_4N^+$) |
| C 1s | 284.8 | 36 | * | 55.5 | 6.83 | R8 & R9 both show a mix of C-C, C-O and COOx |
| Pt 4f | 70.5 | 5.58 | * | 1.75 | 0.32 | Pt metal |

**Method:** X-Ray photoelectron spectra were recorded on an Axis Supra XPS (Kratos Analytical) using a mono-chromated Al Kα source and large area slot mode detector (300x800µm analysis area). Data were recorded using a charge neutralizer to limit differential charging and binding energies were calibrated to the main hydrocarbon peak (BE 284.8 eV). For each etch, a survey scan was recorded using a pass energy of 160eV. A 0.1 eV step size was used when recording the high resolution spectra and a pass energy of 20 eV.