

## **Supporting information**

for

# **How reproducible are electrochemical impedance spectroscopic data for dye-sensitized solar cells?**

**Mariia Becker, Maria-Sophie Bertrams, Edwin C. Constable and Catherine E. Housecroft**

Department of Chemistry, University of Basel, BPR 1096, Mattenstrasse 24a, CH-4058 Basel, Switzerland;  
mariia.karpacheva@unibas.ch (M.B.); maria-sophie.bertrams@stud.unibas.ch (M.-S.B.);  
edwin.constable@unibas.ch (E.C.C.); catherine.housecroft@unibas.ch (C.E.H.)

## Contents

|                                                                                                                                                                  |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| DSC fabrication.....                                                                                                                                             | 3  |
| DSC measurements .....                                                                                                                                           | 3  |
| Table S1. <i>J-V</i> parameters for DSCs with N719 and SQ2 dyes WOPI and API. ....                                                                               | 4  |
| Figure S1. <i>J-V</i> curves for dyes N719 and SQ2 WOPI and API. ....                                                                                            | 4  |
| Table S2. Experimental parameters $\alpha$ and $Q$ needed for the correction of CPE and the final capacitance for DSCs with N719 and SQ2 dyes WOPI and API. .... | 4  |
| Table S3. The EIS parameters for DSCs with N719 dye with fitting model 1. ....                                                                                   | 5  |
| Figure S2. EIS data for DSCs with N719 dye (cells 1-5). ....                                                                                                     | 5  |
| Figure S3. EIS data for DSCs with N719 dye (cells 6-10). ....                                                                                                    | 6  |
| Figure S4. EIS data for DSCs with N719 dye (cells 11-15). ....                                                                                                   | 7  |
| Table S4. <i>J-V</i> parameters for DSCs with N719 dye. ....                                                                                                     | 8  |
| Figure S5. <i>J-V</i> curves for DSCs with N719 dye.....                                                                                                         | 8  |
| Equation S1. Average value. ....                                                                                                                                 | 9  |
| Equation S2. Standard deviation value.....                                                                                                                       | 9  |
| Equation S3. Relative standard deviation value. ....                                                                                                             | 9  |
| Figure S6. EIS data for DSCs with SQ2 dye (cells 1-5). ....                                                                                                      | 10 |
| Figure S7. EIS data for DSCs with SQ2 dye (cells 6-10). ....                                                                                                     | 11 |
| Figure S8. EIS data for DSCs with SQ2 dye (cells 11-15). ....                                                                                                    | 12 |
| Table S5. <i>J-V</i> parameters for DSCs with SQ2 dye. ....                                                                                                      | 13 |
| Figure S9. <i>J-V</i> curves for DSCs with SQ2 dye.....                                                                                                          | 13 |

## DSC fabrication

Each working commercial TiO<sub>2</sub> electrode (opaque, Solaronix) was rinsed with EtOH and dried on a heating plate at 450 °C for 30 min. The electrodes were cooled to 60 °C and dipped in an 0.3 mM EtOH solution of N719 (Solaronix) overnight. In case of SQ2 dye electrodes were immersed in an 0.1 mM CH<sub>2</sub>Cl<sub>2</sub> solution of the dye for 1 h. After soaking in the dye-baths, the electrodes were washed with the same solvent as used in the dye-bath and dried with a heat gun.

Commercial platinum counter electrodes from Solaronix (Test Cell Platinum Electrodes Drilled) were rinsed with EtOH and dried on a heating plate at 450 °C for 30 min. The TiO<sub>2</sub> electrodes and Pt counter-electrodes were assembled together using thermoplast hot-melt sealing foil (Solaronix, Test Cell Gaskets, made from Meltonix 1170-60 sealing film, 60 microns thick) by heating them together. The vacuum backfilling technique was used to introduce the electrolyte into DSCs through a hole drilled in the counter electrode and this was then sealed with a cover glass using hot-melt sealing foil.

## DSC measurements

The solar cell measurements used fully masked cells using black coloured copper sheet with a single aperture placed over the screen printed dye-sensitized TiO<sub>2</sub> square. The area of the aperture in the mask was smaller than the active area of the dye-sensitized TiO<sub>2</sub> (0.36 cm<sup>2</sup>). For complete masking, black cover was also applied over the edges and rear of the cell. Current density-voltage (*J*-*V*) measurements were made by irradiating from the photoanode side with a LOT Quantum Design LS0811 instrument (100 mW cm<sup>-2</sup> = 1 sun at AM 1.5) and the simulated light power was calibrated with a silicon reference cell.

The EQE measurements were performed on a Spe-Quest quantum efficiency setup from ReRa Systems (Netherlands) equipped with a 100W halogen lamp (QTH) and a lambda 300 grating monochromator from Lot Oriel. The monochromatic light was modulated to 1 Hz using a chopper wheel from ThorLabs. The cell response was amplified with a large dynamic range IV converter from CVI Melles Griot and then measured with a SR830 DSP Lock-In amplifier from Stanford Research.

For the EIS measurements a ModuLab<sup>®</sup> XM PhotoEchem photoelectrochemical measurement system from Solartron Analytical was used. The impedance was measured at the open-circuit potential of the cell at a light intensity of 22 mW cm<sup>-2</sup> (590 nm) in the frequency range 0.05 Hz to 100 kHz using an amplitude of 10 mV. The impedance data were analysed and fitted using ZView<sup>®</sup> software from Scribner Associates Inc.

Table S1. *J-V* parameters for DSCs with N719 and SQ2 dyes WOPI and API.

| DSC              | $J_{sc} / \text{mA cm}^{-2}$ | $V_{oc} / \text{mV}$ | $ff / \%$ | $\eta / \%$ |
|------------------|------------------------------|----------------------|-----------|-------------|
| N719 WOPI cell 1 | 14.64                        | 622                  | 68        | 6.17        |
| N719 WOPI cell 2 | 12.84                        | 603                  | 69        | 5.33        |
| N719 API cell 1  | 14.62                        | 621                  | 66        | 6.04        |
| N719 API cell 2  | 12.70                        | 613                  | 67        | 5.24        |
| SQ2 WOPI cell 1  | 1.07                         | 465                  | 70        | 0.35        |
| SQ2 WOPI cell 2  | 1.67                         | 480                  | 71        | 0.57        |
| SQ2 API cell 1   | 1.74                         | 477                  | 71        | 0.58        |
| SQ2 API cell 2   | 2.17                         | 489                  | 72        | 0.77        |

Figure S1. *J-V* curves for dyes N719 and SQ2 WOPI and API.

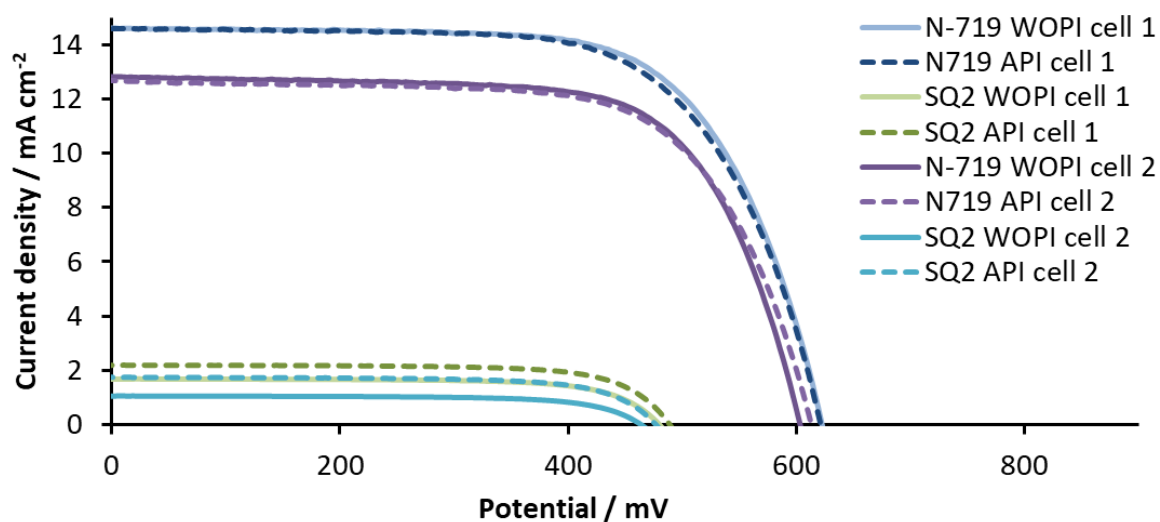


Table S2. Experimental parameters  $\alpha$  and  $Q$  needed for the correction of CPE and the final capacitance for DSCs with N719 and SQ2 dyes WOPI and API.

| DSC <sup>1</sup> | $C_{\mu} / \mu\text{F}$ | $\alpha$ | $Q$    |
|------------------|-------------------------|----------|--------|
| N719 WOPI        |                         |          | 1.2E-3 |
| 0 min            | 845                     | 0.92     |        |
| N719 WOPI        |                         |          | 1.3E-3 |
| 15 min           | 905                     | 0.92     |        |
| N719 WOPI        |                         |          | 1.3E-3 |
| 30 min           | 955                     | 0.91     |        |
| N719 WOPI        |                         |          | 1.4E-3 |
| 45 min           | 981                     | 0.91     |        |
| N719 WOPI        |                         |          | 1.4E-3 |
| 60 min           | 970                     | 0.91     |        |
| SQ2 WOPI         |                         |          | 3.6E-5 |
| 15 min           | 18                      | 0.88     |        |
| SQ2 WOPI         |                         |          | 4.2E-5 |
| 30 min           | 20                      | 0.87     |        |
| SQ2 WOPI         |                         |          | 4.8E-5 |
| 45 min           | 22                      | 0.87     |        |
| SQ2 WOPI         |                         |          | 5.1E-5 |
| 60 min           | 23                      | 0.87     |        |

Table S3. The EIS parameters for DSCs with N719 dye with fitting model 1.

| DSC          | $R_{rec} / \Omega$ | $C_{\mu} / \mu F$ | $\alpha$ | $\tau / ms$ | $W_s / \Omega$ | $R_s / \Omega$ | $R_{Pt} / \Omega$ | $C_{Pt} / \mu F$ |
|--------------|--------------------|-------------------|----------|-------------|----------------|----------------|-------------------|------------------|
| N719 cell 1  | 25                 | 759               | 0.93     | 19          | 12             | 11             | 11                | 4                |
| N719 cell 2  | 22                 | 724               | 0.95     | 16          | 11             | 11             | 8                 | 4                |
| N719 cell 3  | 24                 | 902               | 0.94     | 22          | 9              | 14             | 7                 | 4                |
| N719 cell 4  | 22                 | 853               | 0.94     | 19          | 10             | 11             | 8                 | 5                |
| N719 cell 5  | 25                 | 850               | 0.93     | 22          | 11             | 10             | 8                 | 5                |
| N719 cell 6  | 24                 | 972               | 0.94     | 24          | 9              | 11             | 6                 | 5                |
| N719 cell 7  | 25                 | 957               | 0.95     | 24          | 14             | 14             | 7                 | 4                |
| N719 cell 8  | 23                 | 934               | 0.94     | 21          | 11             | 10             | 9                 | 4                |
| N719 cell 9  | 28                 | 955               | 0.94     | 26          | 11             | 9              | 7                 | 5                |
| N719 cell 10 | 27                 | 828               | 0.93     | 22          | 11             | 14             | 12                | 4                |
| N719 cell 11 | 22                 | 756               | 0.94     | 17          | 10             | 11             | 8                 | 4                |
| N719 cell 12 | 17                 | 810               | 0.96     | 14          | 9              | 12             | 6                 | 4                |
| N719 cell 13 | 23                 | 670               | 0.95     | 16          | 10             | 10             | 7                 | 5                |
| N719 cell 14 | 25                 | 718               | 0.94     | 18          | 10             | 10             | 8                 | 4                |
| N719 cell 15 | 29                 | 615               | 0.95     | 18          | 9              | 11             | 7                 | 4                |

Figure S2. EIS data for DSCs with N719 dye (cells 1-5).

Solid lines represent fitted curves, dotted lines represent experimental data. (a) Nyquist plots, the expansion shows the high frequency region. (b) Bode plot.

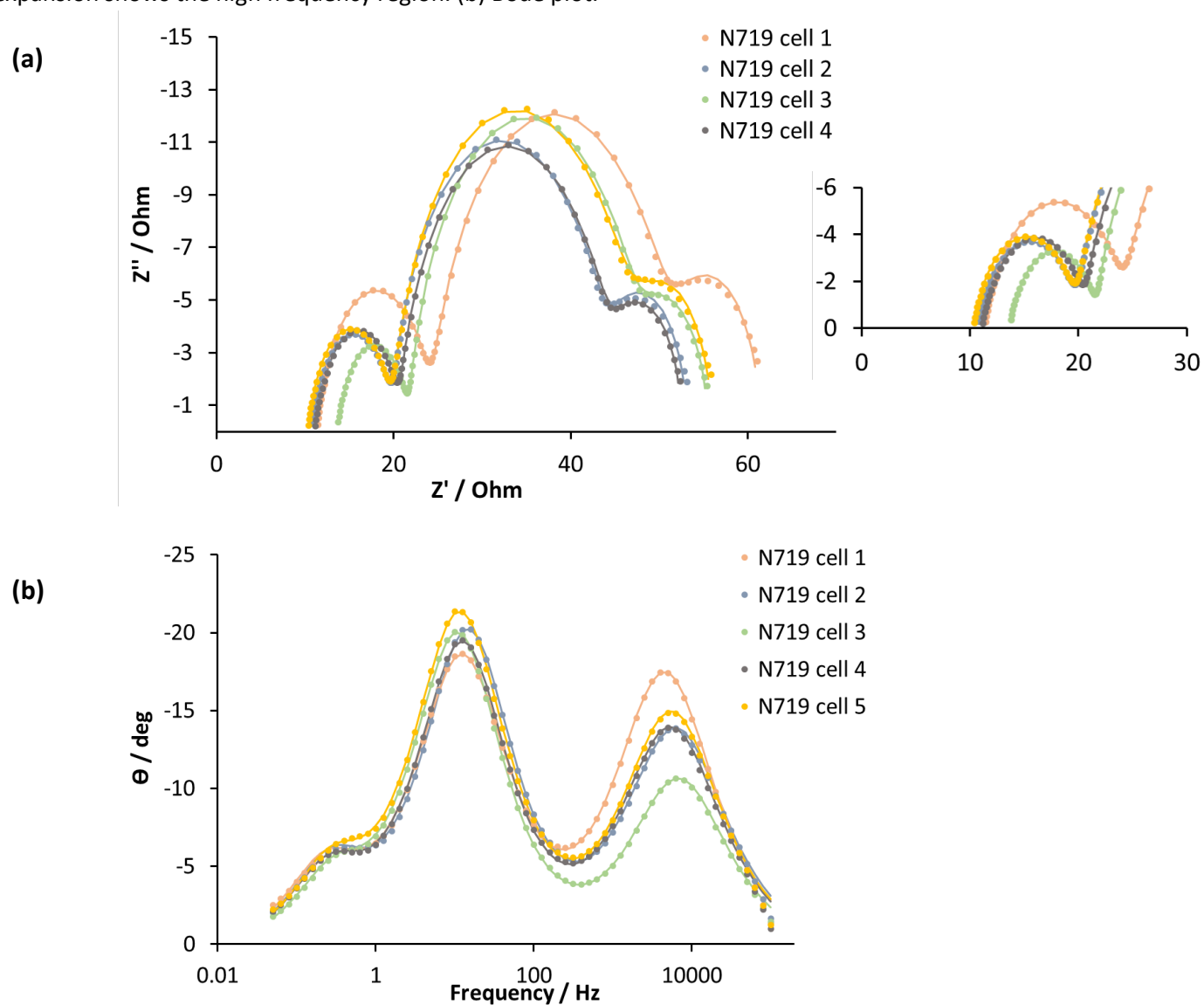


Figure S3. EIS data for DSCs with N719 dye (cells 6-10).

Solid lines represent fitted curves, dotted lines represent experimental data. (a) Nyquist plots, the expansion shows the high frequency region. (b) Bode plot.

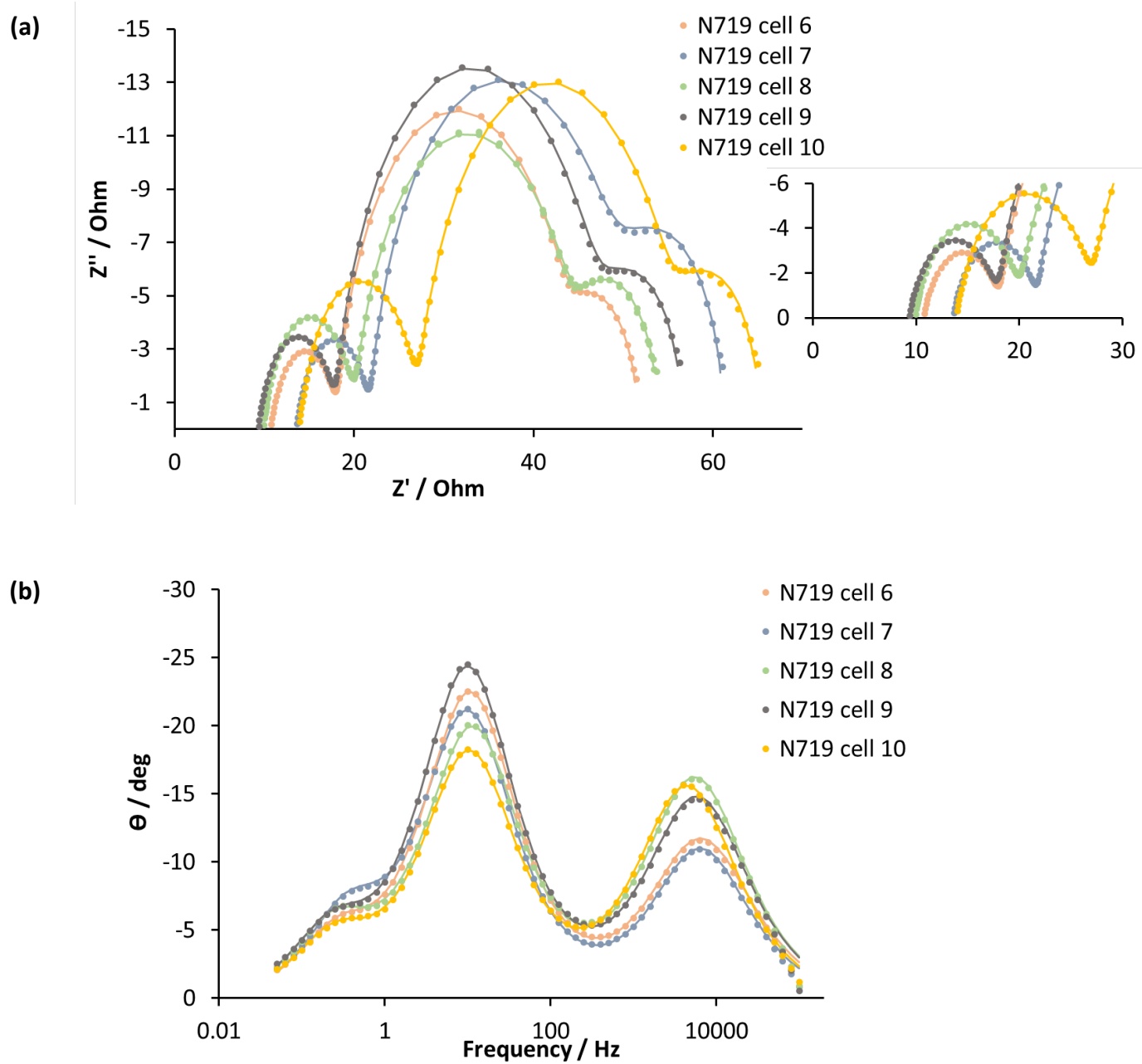


Figure S4. EIS data for DSCs with N719 dye (cells 11-15).

Solid lines represent fitted curves, dotted lines represent experimental data. (a) Nyquist plots, the expansion shows the high frequency region. (b) Bode plot.

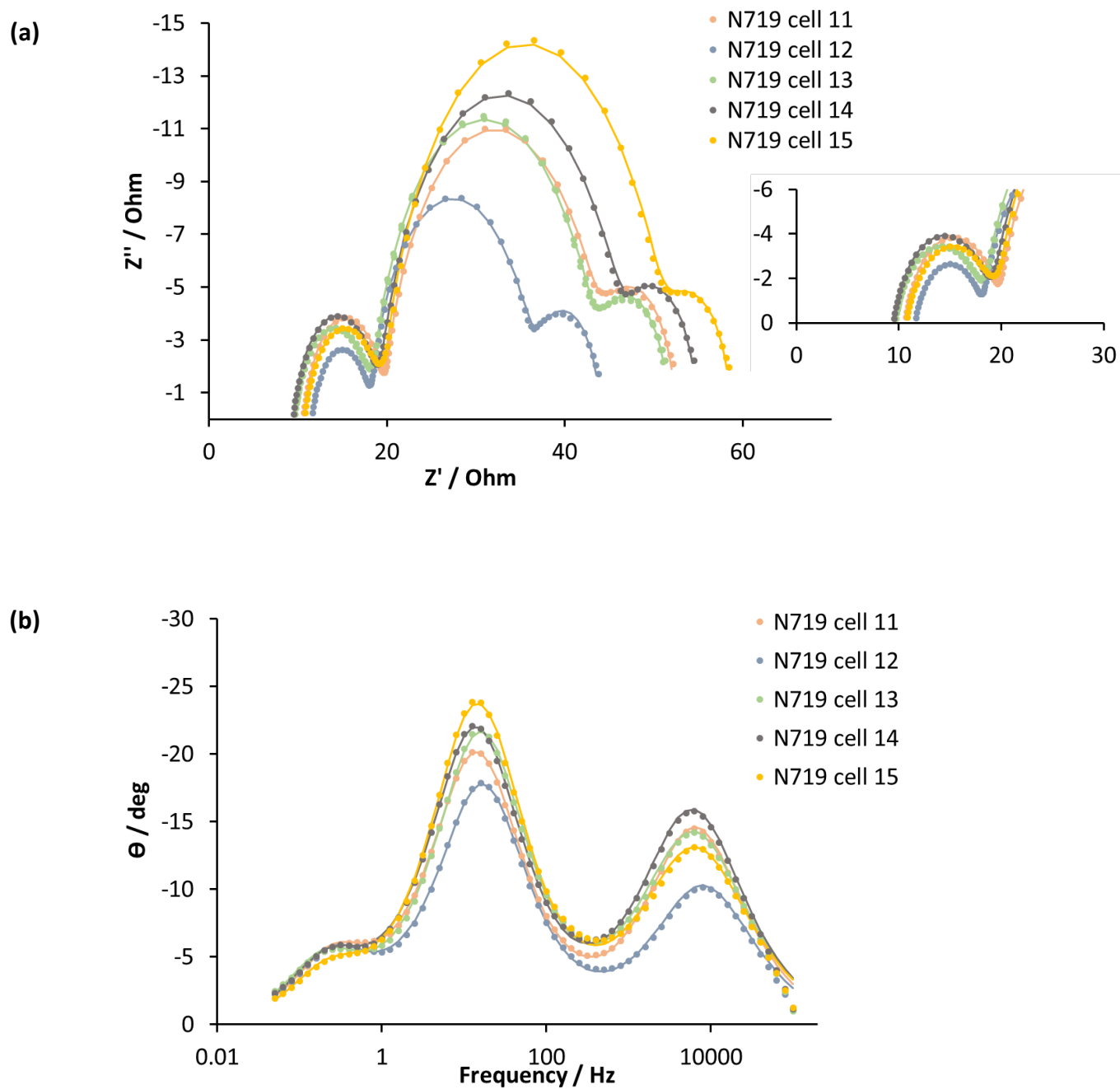
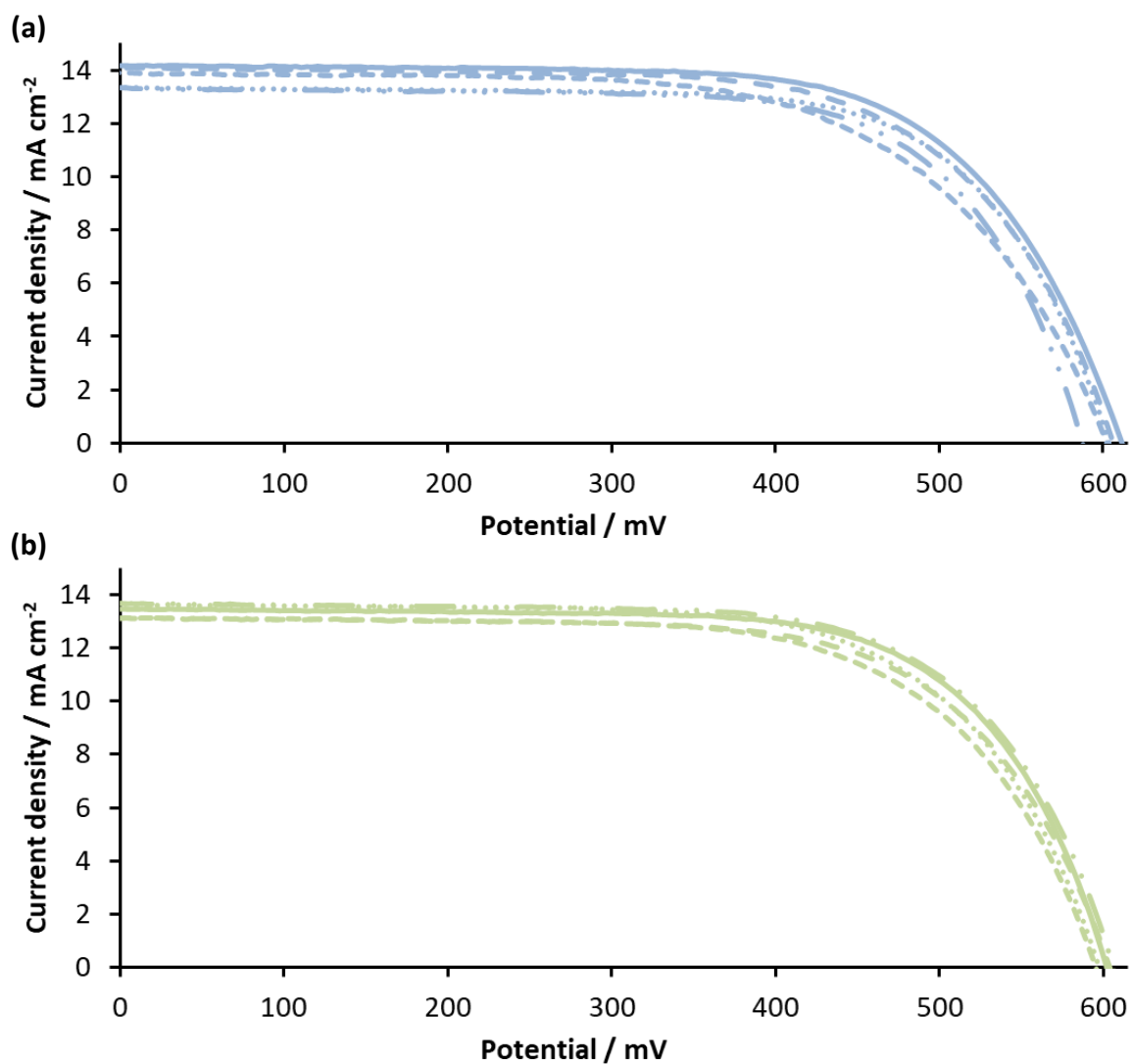


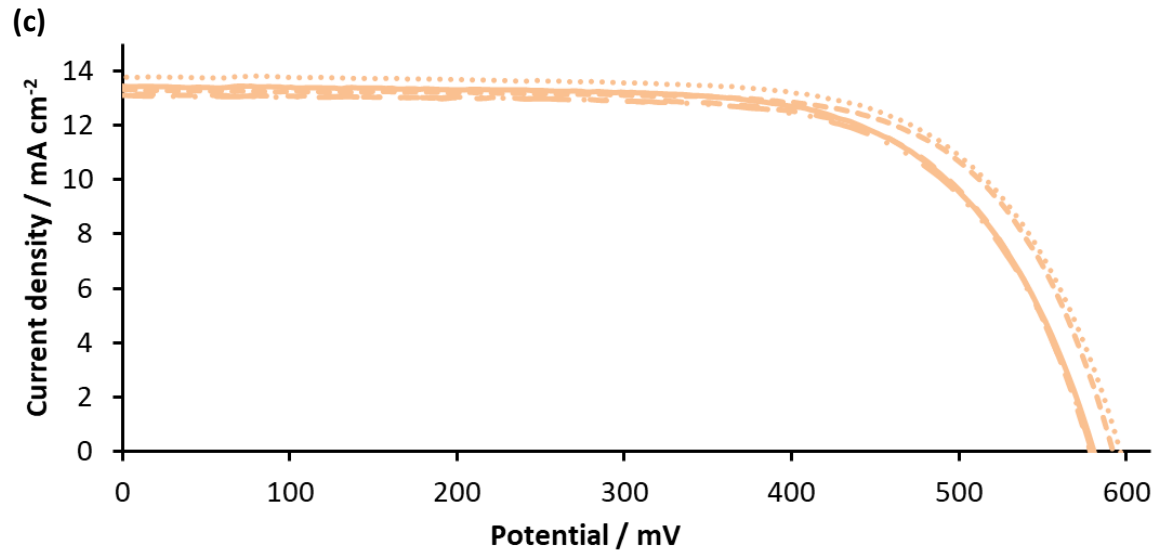
Table S4. *J-V* parameters for DSCs with N719 dye.

| DSC          | $J_{sc} / \text{mA cm}^{-2}$ | $V_{oc} / \text{mV}$ | $ff / \%$ | $\eta / \%$ |
|--------------|------------------------------|----------------------|-----------|-------------|
| N719 cell 1  | 13.37                        | 604                  | 69        | 5.59        |
| N719 cell 2  | 13.33                        | 588                  | 69        | 5.41        |
| N719 cell 3  | 14.19                        | 611                  | 67        | 5.85        |
| N719 cell 4  | 13.94                        | 602                  | 63        | 5.25        |
| N719 cell 5  | 14.12                        | 606                  | 66        | 5.67        |
| N719 cell 6  | 13.49                        | 602                  | 69        | 5.59        |
| N719 cell 7  | 13.15                        | 595                  | 66        | 5.13        |
| N719 cell 8  | 13.65                        | 597                  | 66        | 5.41        |
| N719 cell 9  | 13.70                        | 606                  | 68        | 5.64        |
| N719 cell 10 | 13.14                        | 603                  | 67        | 5.31        |
| N719 cell 11 | 13.46                        | 581                  | 68        | 5.28        |
| N719 cell 12 | 13.18                        | 578                  | 69        | 5.27        |
| N719 cell 13 | 13.30                        | 592                  | 70        | 5.54        |
| N719 cell 14 | 13.83                        | 597                  | 69        | 5.67        |
| N719 cell 15 | 13.13                        | 579                  | 68        | 5.20        |

Figure S5. *J-V* curves for DSCs with N719 dye.

(a) Cells 1-5, (b) cells 6-10; (c) cells 11-15.





Equation S1. Average value.

$$average = \frac{x_1 + x_2 + \dots + x_n}{n}$$

Equation S2. Standard deviation value.

$$SD = \sqrt{\frac{1}{n} \sum_{i=1}^n (n_i - n_{average})^2}$$

Equation S3. Relative standard deviation value.

$$RSD = \frac{SD}{average} * 100$$

Figure S6. EIS data for DSCs with SQ2 dye (cells 1-5).

Solid lines represent fitted curves, dotted lines represent experimental data. (a) Nyquist plots, the expansion shows the high frequency region. (b) Bode plot.

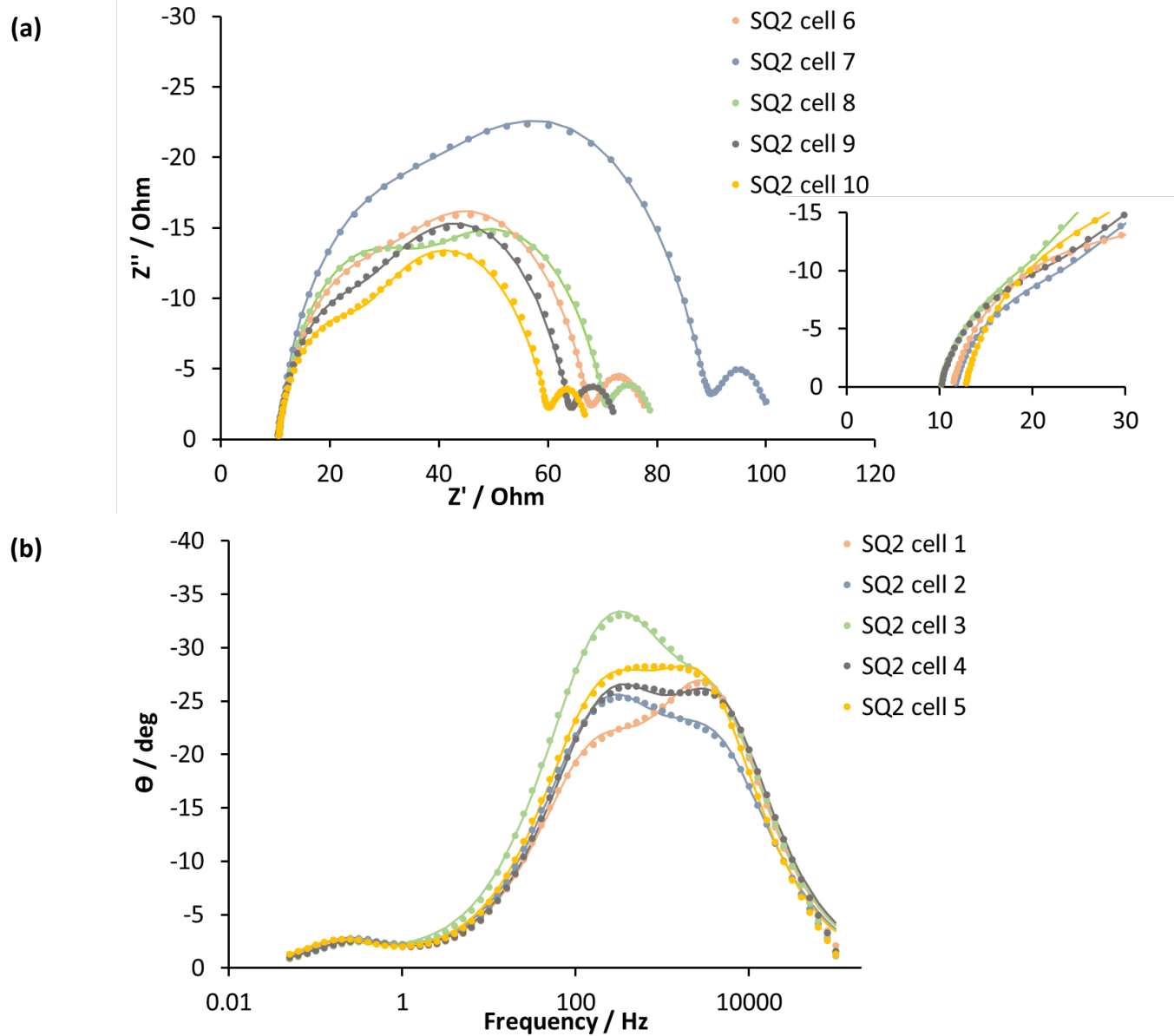


Figure S7. EIS data for DSCs with SQ2 dye (cells 6-10).

Solid lines represent fitted curves, dotted lines represent experimental data. (a) Nyquist plots, the expansion shows the high frequency region. (b) Bode plot.

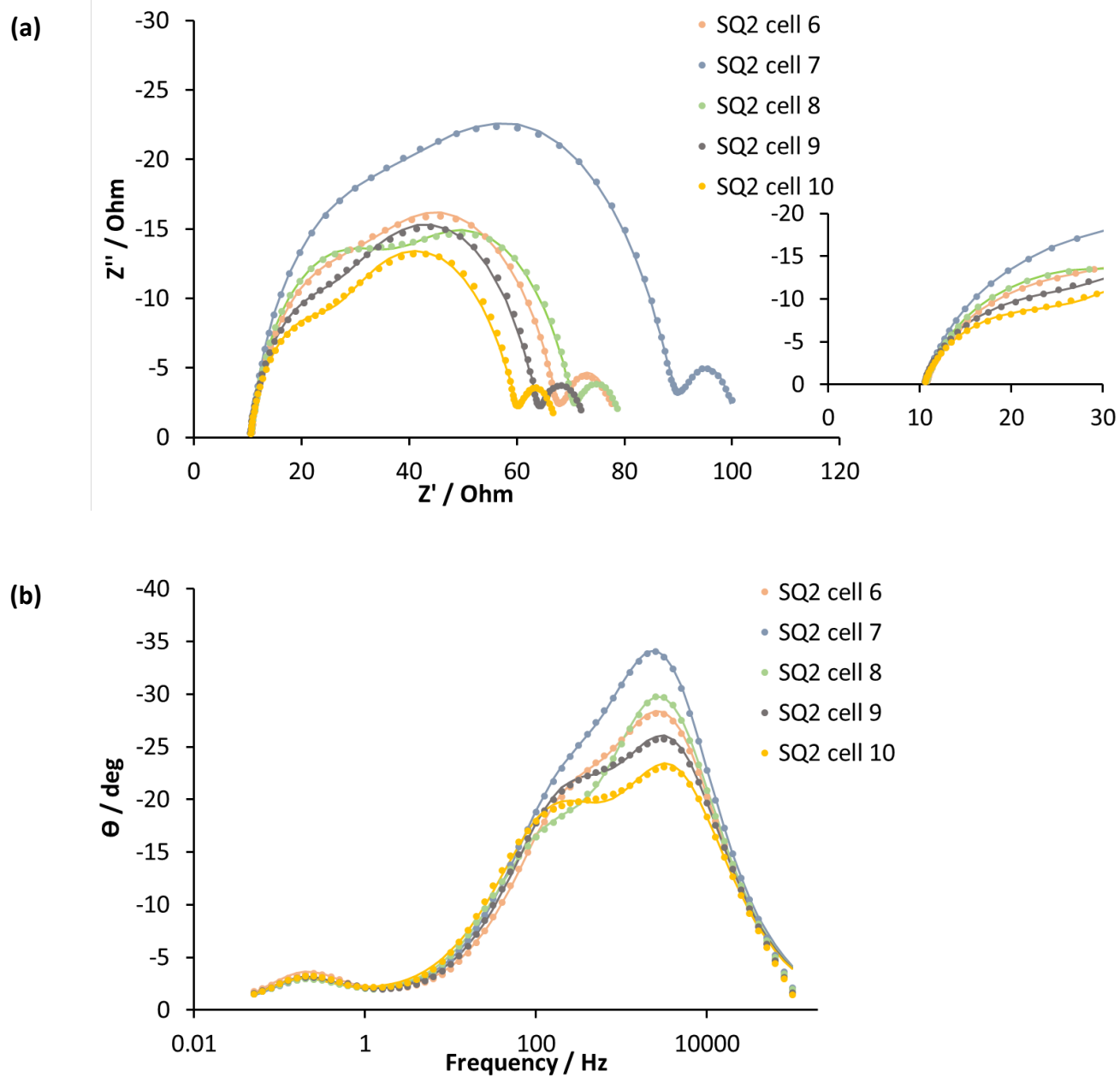


Figure S8. EIS data for DSCs with SQ2 dye (cells 11-15).

Solid lines represent fitted curves, dotted lines represent experimental data. (a) Nyquist plots, the expansion shows the high frequency region. (b) Bode plot.

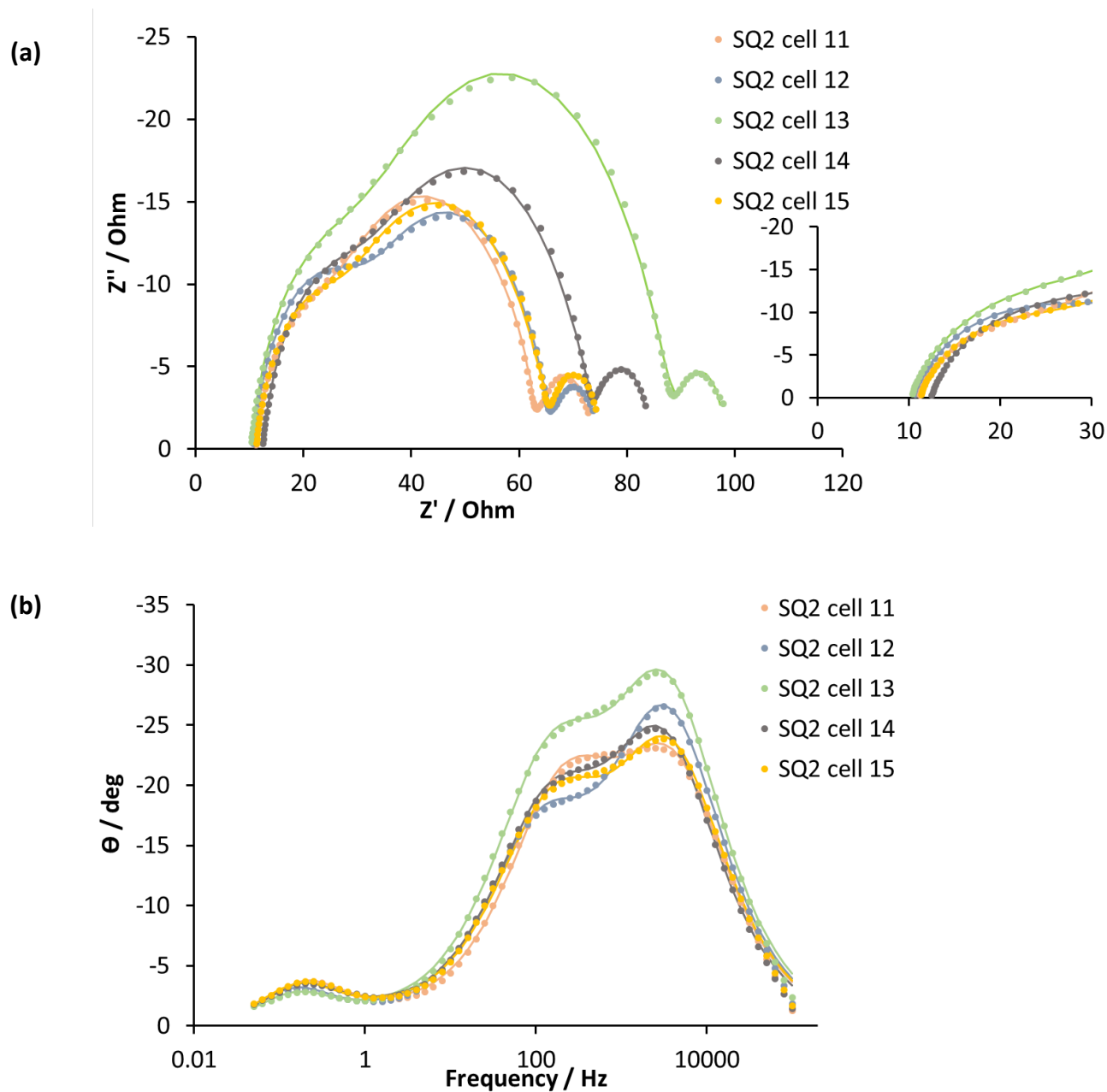


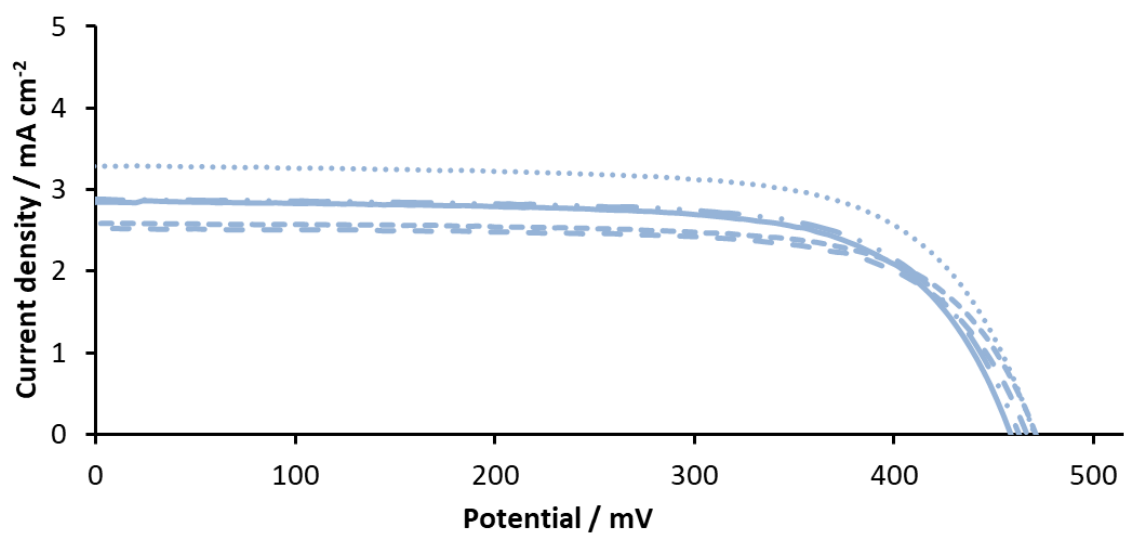
Table S5. *J-V* parameters for DSCs with SQ2 dye.

| DSC         | $J_{sc} / \text{mA cm}^{-2}$ | $V_{oc} / \text{mV}$ | $ff / \%$ | $\eta / \%$ |
|-------------|------------------------------|----------------------|-----------|-------------|
| SQ2 cell 1  | 2.85                         | 458                  | 69        | 0.9         |
| SQ2 cell 2  | 2.59                         | 471                  | 70        | 0.86        |
| SQ2 cell 3  | 2.52                         | 466                  | 71        | 0.83        |
| SQ2 cell 4  | 3.29                         | 470                  | 69        | 1.06        |
| SQ2 cell 5  | 2.88                         | 463                  | 69        | 0.92        |
| SQ2 cell 6  | 3.97                         | 486                  | 70        | 1.35        |
| SQ2 cell 7  | 2.84                         | 466                  | 68        | 0.91        |
| SQ2 cell 8  | 3.31                         | 479                  | 70        | 1.1         |
| SQ2 cell 9  | 3.65                         | 484                  | 68        | 1.2         |
| SQ2 cell 10 | 2.94                         | 473                  | 70        | 0.98        |
| SQ2 cell 11 | 3.77                         | 479                  | 69        | 1.24        |
| SQ2 cell 12 | 3.23                         | 502                  | 72        | 1.17        |
| SQ2 cell 13 | 2.27                         | 484                  | 72        | 0.79        |
| SQ2 cell 14 | 2.14                         | 487                  | 72        | 0.75        |
| SQ2 cell 15 | 3.83                         | 496                  | 72        | 1.36        |

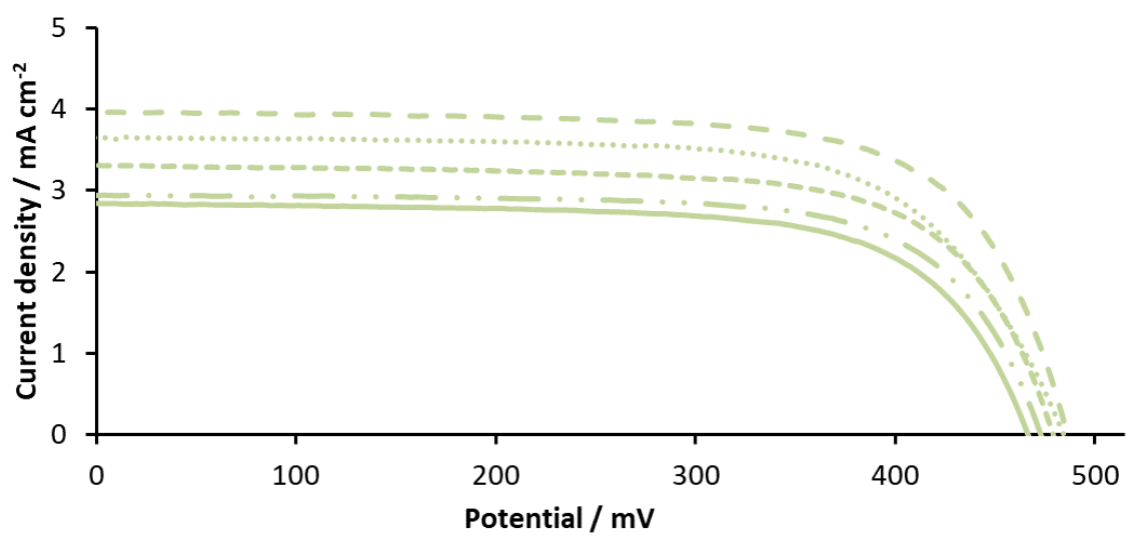
Figure S9. *J-V* curves for DSCs with SQ2 dye.

(a) Cells 1-5, (b) cells 6-10; (c) cells 11-15.

(a)



(b)



(c)

