

## Supplementary Information for

# Organic dye-sensitized solar cells containing alkaline iodide-based gel polymer electrolytes: influence of cation size

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## Table of Contents

|                                                                                                               |    |
|---------------------------------------------------------------------------------------------------------------|----|
| 1. Determination of the amount of adsorbed dye <b>D35</b> .....                                               | S2 |
| 2. EIS spectra of electrolyte samples containing the different alkaline cations.....                          | S2 |
| 3. Fitting of transmission FT-IR spectra of PAN/EC/PC electrolytes containing different alkaline cations..... | S4 |
| 4. References.....                                                                                            | S6 |

## 1. Determination of the amount of adsorbed dye D35

The amount of adsorbed **D35** dye in terms of moles per square centimeter of dyed film was obtained from UV-Vis absorption data of dye films using the following formula

$$A = 1000 \cdot \varepsilon \cdot \Gamma$$

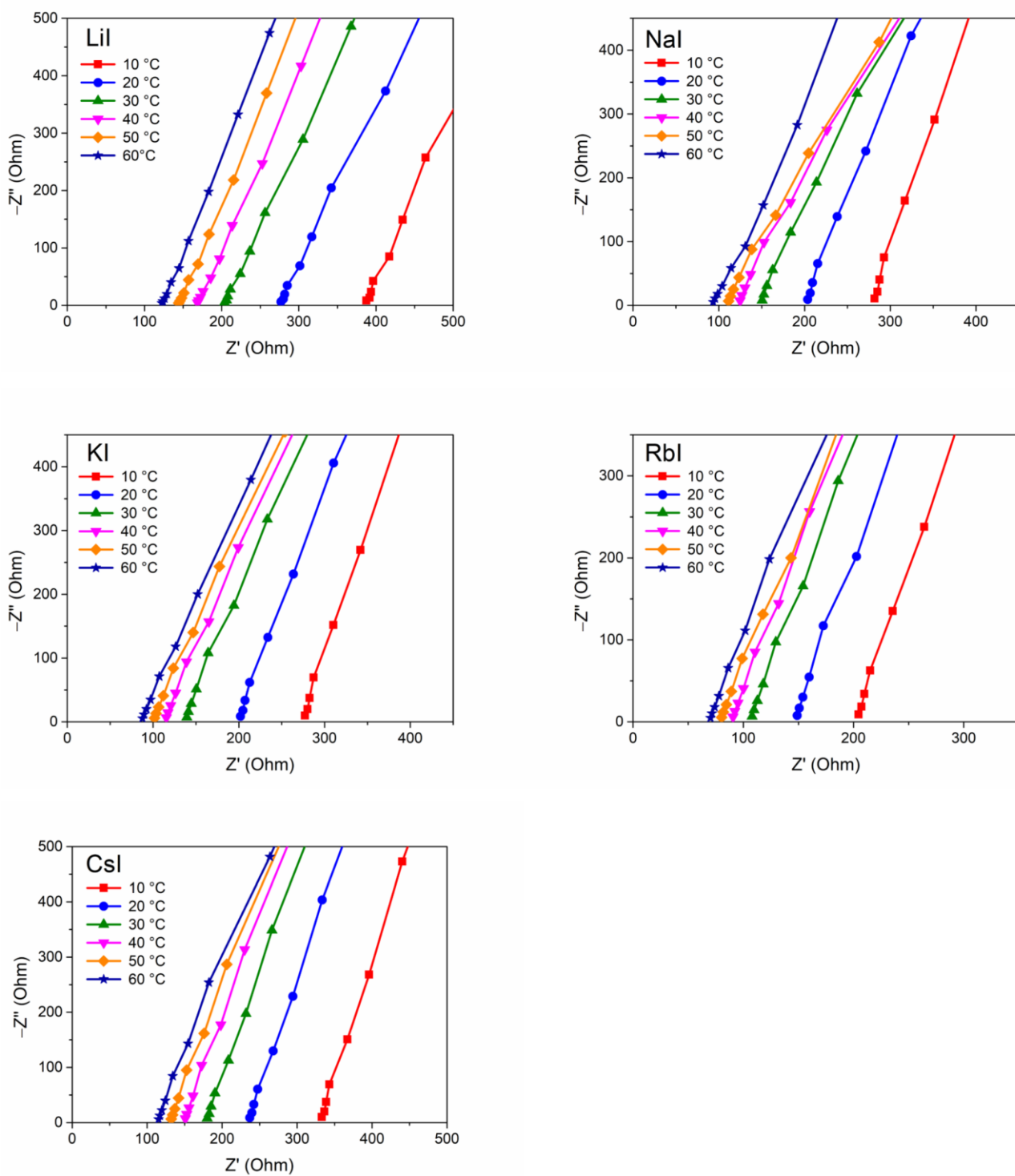
where  $A$  is the absorbance,  $\varepsilon$  is molar extinction coefficient ( $\text{M}^{-1} \text{cm}^{-1}$ ) and  $\Gamma$  ( $\text{mol cm}^{-2}$ ) the dye coverage on the film.<sup>[1]</sup> The value of  $\varepsilon$  ( $17\,000 \text{ M}^{-1} \text{cm}^{-1}$  at 450 nm) for **D35** was taken from ref. [2].

## 2. EIS spectra of electrolyte samples containing the different alkaline cations

EIS spectra were recorded on gel electrolyte samples with a diameter of ~6 mm and the following thickness values: LiI, 1.8 mm; NaI, 1.8 mm; KI, 2.1 mm; RbI, 1.6 mm; CsI, 2.7 mm. Samples were sandwiched between two stainless steel (SS) electrodes, and measurements were carried out using a computer-controlled HP4274 impedance analyzer in the frequency range 10 Hz-0.1 MHz, in the temperature range 10-60 °C. Bulk ionic conductivities ( $\sigma$ ) of the different electrolytes were calculated based on the intercept with the real axis of the Nyquist plots, using the following equation:

$$\sigma = \frac{1}{\rho} \quad \text{with: } \rho = R \cdot \frac{A}{l}$$

where  $\rho$  is the resistivity of the samples,  $R$  is their resistance (intercept with the real axis of the Nyquist plot),  $A$  is their surface area and  $l$  is their thickness. Nyquist plots for the five samples are shown in Figure S1. Only the linear parts and not the semicircular parts of the curves were visible within the measured frequency range.

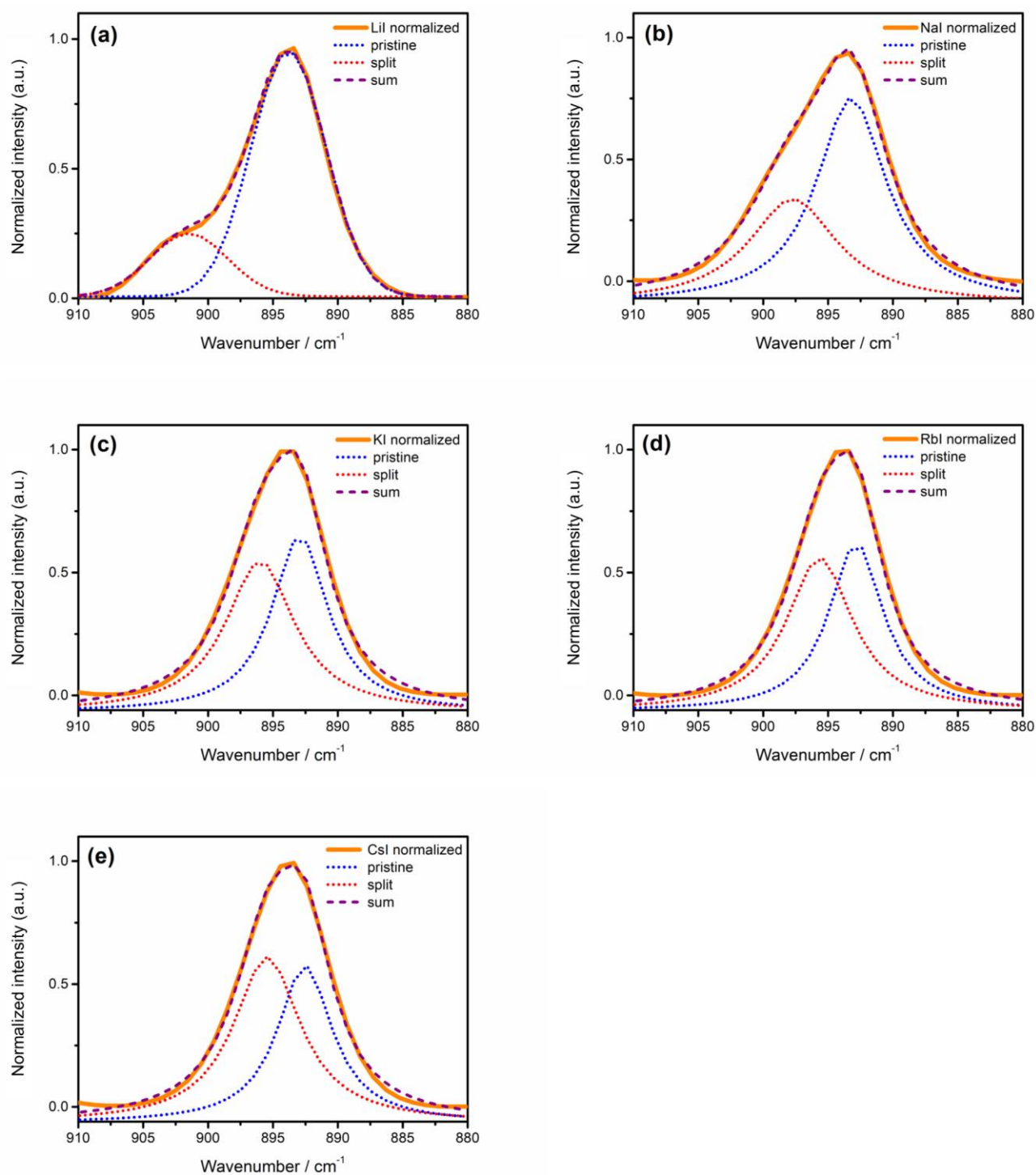


**Figure S1.** Nyquist plots of the EIS spectra recorded for the different alkaline iodide-containing electrolytes in the 10-60 °C range.

### **3. Fitting of transmission FT-IR spectra of PAN/EC/PC electrolytes containing different alkaline cations**

Transmission FT-IR spectra of the different gel electrolytes used in this study were baseline corrected and normalized relative to the EC ring breathing mode around  $893\text{ cm}^{-1}$ , and the latter band was subjected to a fitting procedure to highlight the intensity and the position of the split peak generated upon EC coordination by the alkaline cations. Deconvolution was carried out with Origin 9.0 Software (OriginLab) using the multiple (2) peak automatic fitting, employing Lorentzian functions and an initial  $4\text{ cm}^{-1}$  band width, for all samples, except the LiI sample where Gaussian functions were used. The change of method (Lorentzian  $\rightarrow$  Gaussian) was forced by the difference of shape of the two peaks in the LiI sample. As a result of the deconvolution process, the position of the pristine band was found to change slightly by  $\pm 1\text{ cm}^{-1}$ , providing the magnitude of the peak position error in the fitting procedure.

The outcome of the deconvolution process for the five different alkaline iodide-containing electrolytes is shown in Figure S2.



**Figure S2.** Fitting of the normalized transmission FT-IR spectra of the different gel electrolytes around the  $893\text{ cm}^{-1}$  EC ring breathing band. (a) LiI; (b) NaI; (c) KI; (d) RbI; (e) CsI.

#### 4. References

- [1] M. Pazoki, P. W. Lohse, N. Taghavinia, A. Hagfeldt, G. Boschloo, *Phys. Chem. Chem. Phys.* **2014**, *16*, 8503.
- [2] X. Jiang, K. M. Karlsson, E. Gabrielsson, E. M. J. Johansson, M. Quintana, M. Karlsson, L. Sun, G. Boschloo, A. Hagfeldt, *Adv. Funct. Mater.* **2011**, *21*, 2944.