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Supplementary Information

Optical study of electrochromic moving fronts for the investigation of ion transport in conducting polymers

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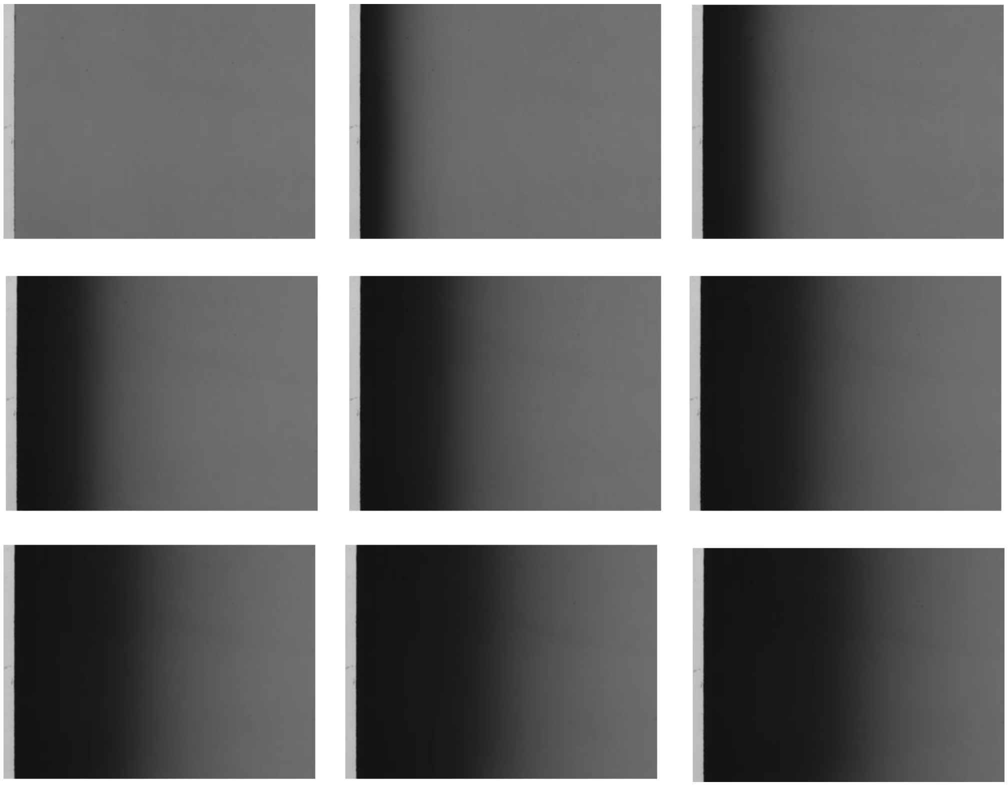

Figure S1. Time lapse images representing the evolution of the dedoping front in PEDOT:PSS film (0 vol% EG) during the injection of K^+ cations upon application of 2V. The time interval is 5s and the first image corresponds to the zero bias state.

The fitting procedure accounts for a full least squares fit of the Spano model.[25] In this case, the entirety of the data (multiple time points for the two PEDOT:PSS formulations chosen, spectra shown in Figure S2) are fit with the same E_{00}=1.81 eV, and E_p=0.176eV (slightly lower than the expected C=C ring breathing mode) to reduce the number of free fit parameters. The Huang Rhys parameter is fixed to S=1. In this work the entire dataset is first fit to the aggregate region of the spectrum (~1.6-2.0 eV), to obtain the residual spectra in the amorphous absorption region (2-3 eV), which are then normalized and averaged. The fit is iterative in that the averaged residual in this region is now used in the full fit to account for the approximate amorphous absorption. The fit results shown in Supplementary Figure S3 are the data, the vibronic progression attributed to aggregate absorption, and the difference between the two. Note that this treatment results in residual spectra of the amorphous region that are self-consistent. In the main text, we assume that the case of PEDOT is similar to that of P3HT (where the increase in oscillator strength going from the amorphous to the aggregated phase is ~39%),[45] as a means to estimate the % aggregates. We reiterate that such an assumption is not critical, as we do not attempt to quantify the absolute aggregate fraction in the film, but merely to show the time-dependent progression of the relative absorption of aggregated *vs*. amorphous content subject to interaction with drifting K^+ ions.

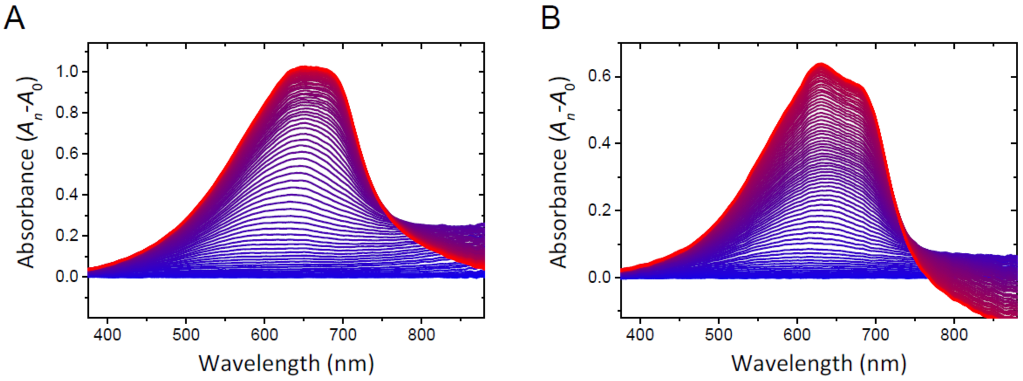

Figure S2. Absorbance spectra of PEDOT:PSS film cast with 0 vol% (**A**), and 50 vol% (**B**) EG content in PEDOT:PSS formulation (*X*=4mm from electrolyte/film interface). The data used to plot these time dependent spectra, are the same as those used to fit and extract parameters presented in the main text, Figure 3.

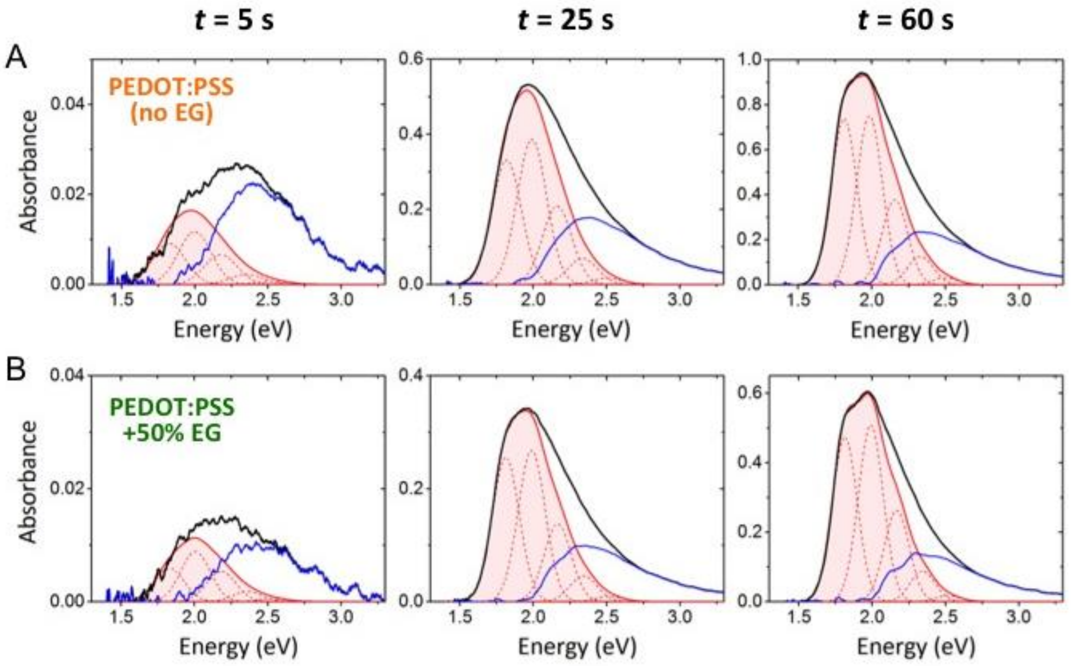

Figure S3. Absorbance spectra at *t*=5s, 25s, and 60s of (**A**) PEDOT:PSS and (**B**) PEDOT:PSS+50 vol% EG films during a moving front experiment (*X*=4mm from electrolyte/film interface). The background subtracted absorbance spectra (black) are shown with the fit aggregate spectra (red), and the residual absorbance contribution (blue) stemming from disordered/amorphous content in the film.