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# Supplementary Information

Role of aggregates and microstructure of mixed-ionic-electronic-conductors on charge transport in electrochemical transistors

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# S1 Methods

### S1.1 Optical Absorption peak fitting

Absorption is reported as:

$$Abs_{10} = -log_{10}\left(\frac{I}{I_0}\right) \tag{S1}$$

where, I is the transmitted light intensity through a sample, and  $I_0$  is the transmitted light intensity through a reference sample (ITO on glass in this case).

Optical absorption data were fit to the vibronic model developed by Spano et al. [1]. This model is based on a modified Holstein Hamiltonian that treats the homopolymer aggregates as a molecular crystal with a single phonon mode responsible for electron-phonon coupling. The model predicts absorption according to Equation S2 as a sum of individual vibronic transitions.

$$A(\omega) = C \sum_{m=0}^{\infty} \frac{e^{-\lambda^2} \lambda^{2m}}{m!} \left( 1 - \frac{W e^{-\lambda^2}}{2E_p} G(\lambda^2; m) \right)^2 \Gamma(\hbar\omega - E_{00} - mE_p - 0.5W \lambda^{2m} e^{-\lambda^2})$$
(S2)

where

$$G(\lambda^2;m) = \sum_{\substack{n=0,1...\\n \neq m}} \frac{\lambda^{2n}}{n!(n-m)}$$
(S3)

and the lineshape function is given by a Gaussian

$$\Gamma(X) = \frac{1}{\sigma(2\pi)^{\frac{1}{2}}} e^{\frac{-X^2}{2\sigma^2}}$$
(S4)

The free parameters in the fit are the exciton bandwidth (W), the 0-0 vibronic transition energy  $(E_{00})$ , the absorption peak linewidth ( $\sigma$  in the Gaussian linewidth function  $\Gamma$ ), and the scaling factor C.  $\lambda^2$  represents the Huang-Rhys factor.  $\lambda^2 \sim 1$  for interacting chain segments, and this value is estimated to within  $\sim 5\%$  [2]. In this work, we used  $\lambda^2 = 0.95$  to keep all exciton bandwidth values positive. More details on this choice are given in Section S1.2. Ep is the vibrational energy of the single phonon mode that is responsible for electron-phonon coupling. This phonon mode is taken to be the symmetric thiophene backbone ring-breathing mode ( $Ep \sim 0.17$  eV). This "single" mode is a complex mixture of multiple phonon modes, but the vibronic model can nonetheless work by combining these modes into a single ensemble average. In this work, Ep was kept constant at 0.169 eV and 0.160 eV for polymer p(g3T2) and p(g2T2), respectively. These values were determined by performing fits of fully reduced polymer spectra (polymer charged to -0.5V vs. Ag/AgCl in 0.1M NaCl aqueous electrolyte) and allowing Ep to vary until a minimum  $\chi^2$  of the fit was determined. The absorption sum was performed from m = 0 to m = 4, corresponding to fitting the 0-0, 0-1, 0-2, 0-3, and 0-4 vibronic transitions. The fits were performed using the Levenberg-Marquardt algorithm with modifications according to Fletcher [3]. The fitted data was constrained to a subset of the experimental data to capture the dominant aggregate absorption components. For polymer p(g3T2), the standard UV-Vis absorbance was fit in the range of 1.650 to 1.930 eV and the differential UV-Vis absorbance was fit in the range of 1.5 to 0.193 eV. For polymer p(g2T2), the standard UV-Vis absorbance was fit in the range of 1.700 to 0.190 eV and the differential UV-Vis absorbance was fit in the range of 1.5 to 1.980 eV.

For fits to differential absorbance spectra, a single gaussian term was added to capture features of polaron absorption (i.e. the positive features in the  $\Delta A$  spectra). Polaronic absorption features are expected to introduce a series of subbandgap states [4, 5], but we make no attempt to fit multiple polaron absorption peaks due to 1) lack of information at photon energies below ~ 1.2 eV due to limitations in the spectral throughput of our spectroelectrochemical setup and 2) lack of constraints on polaron peak fit requirements. The gaussian term added modifies Equation S2 with the following addition:

$$-C_{pol} e^{-\frac{(\hbar\omega - E_{pol})^2}{2\sigma_{pol}^2}}$$
(S5)

where  $C_{pol}$  is the scale of the polaron peaks,  $E_{pol}$  is the polaron transition energy, and  $\sigma_{pol}$  is the breadth of the polaron peak.

Aggregate fraction, F, is found by taking the ratio of the integrated spectral intensity of the vibronic fits according to Equation S2  $(A_{agg}(\omega))$  and the integrated spectral intensity of the vibronic fit subtracted from the experimental data (i.e. the "amorphous" absorbance,  $A_{amor}(\omega)$ ), weighted by the molar extinction coefficients for the aggregate absorbance  $(\epsilon_{agg})$  and the amorphous absorbance  $(\epsilon_{amor})$ . The vibronic fit and the amorphous absorbance are integrated over the region of 1.6 eV to 3.2 eV to yield the aggregate fraction shown in Equation S6.

$$F = \frac{\epsilon_{agg} \int A_{agg}(\omega) d\omega}{\epsilon_{amor} \int A_{amor}(\omega) d\omega + \epsilon_{agg} \int A_{agg}(\omega) d\omega}$$
(S6)

Values from P3HT are used to estimate the relative magnitude of  $\epsilon_{agg}$  and  $\epsilon_{amor}$ , where  $\epsilon_{agg} = 1.39 \epsilon_{amor}$  as found in Ref. [6].

#### **S1.2** Relating $R_{00/01}$ to W and Selecting $\lambda^2$

The ratio of the first two lowest energy vibronic absorption peaks, the 0-0 and 0-1 transitions, is given by  $R_{00/01}$ 

$$R_{00/01} = \frac{I_{00}}{I_{01}} \tag{S7}$$

where  $I_{00}$  and  $I_{01}$  are the integrated intensities of the 0-0 and 0-1 transitions as found from fits of Equation S2 to UV-Vis absorbance data. References [7] and [8] show that  $R_{00/01}$  is linked W by Equation S8

$$R_{00/01} \approx \frac{\left(1 - G(\lambda^2; 0)e^{-\lambda^2} W/(2E_p)\right)^2}{\lambda^2 \left(1 - G(\lambda^2; 1)e^{-\lambda^2} W/(2E_p)\right)^2}$$
(S8)

 $G(\lambda^2; 0)$  and  $G(\lambda^2; 1)$  are given by Equation S3. Evaluating Equation S8 with  $\lambda^2 = 1$  as typically chosen for weakly interacting H-aggregates [1, 6], directly links  $R_{00/01}$  to W by Equation S9:

$$R_{00/01} \approx \frac{\left(1 - 0.24 \, W/(E_p)\right)^2}{\left(1 + 0.073 \, W/(E_p)\right)^2} \qquad \lambda^2 = 1 \tag{S9}$$

However, Equation S9, with  $\lambda^2 = 1$ , results in calculated negative W for  $R_{00/01} > 1$ . Since  $W = 4J_{inter}$ , where  $J_{inter}$  represents the interchain exciton coupling and is always positive for conjugated polymer  $\pi$ -stacks, W is only physically meaningful for H-aggregates if positive [7]. If  $R_{00/01}$  becomes larger than unity by > 10%, the use of a weakly interacting H-aggregate model would need to be reconsidered, and an HJ-aggregate model would likely need to be employed [7, 8]. However, the HJ-aggregate model introduces additional uncertainties in the selection of  $\lambda^2$  and both interchain and intrachain exciton coupling. In this work, we find a maximum  $R_{00/01}$  value of 1.04 for p(g3T2) differential absorbance data at  $n \sim 3 \times 10^{20}$  cm<sup>-3</sup> (Figure 3d). Though greater unity, this  $R_{00/01}$  value sits within the range of values for which the error of  $\lambda^2$  (error  $\sim 5\%$ ) can still account for H-aggregate behavior. Based on this error, we performed trial calculations of Equation S8 using different  $\lambda^2$  choices ranging from  $\lambda^2 = 0.95$  to  $\lambda^2 = 1$ . Table S1 shows how the exact choice of  $\lambda^2$  for Equation S8 evaluated at  $R_{00/01} = 1.04$  yields slightly different W. Table S1 also shows the vibronic factors ( $G(\lambda^2; 0)$  and  $G(\lambda^2; 1)$ ) evaluated according to Equation S3 for the various choices of  $\lambda^2$ . Note, for  $\lambda^2 = 1$ , Equation S9 is recovered. Importantly, Table S1 highlights that the choice of the Huang-Rhys factor within the range of reasonable values ( $\lambda^2 = 1 \pm 0.05$ ) will certainly lead to minor impacts on the calculated exciton bandwidths, though we emphasize that this does not change the observed bandwidth trends shown in Figure 3d. The key finding of Figure 3d remains that electronic charges occupy regions with decreasing exciton interchain coupling, a feature of relatively long interacting conjugation lengths.

Table S1: W for various choices of  $\lambda^2$  evaluated at  $R_{00/01} = 1.04$ 

$\lambda^2$	$G(\lambda^2; 0)e^{-\lambda^2}$	$G(\lambda^2; 1)e^{-\lambda^2}$	W [meV]
0.95	0.4769	-0.1795	3.4
0.96	0.4786	-0.1730	0.4
0.97	0.4802	-0.1665	-2.4
0.98	0.4818	-0.1600	-5.0
0.99	0.4833	-0.1536	-7.6
1.00	0.4848	-0.1473	-10.0

#### S1.3 GIWAXS Beamline Setup and Data Processing

GIWAXS data was collected using an area detector (Rayonix MAR-225) and incident energy of 12.73 keV. The distance between sample and detector was calibrated using a LaB6 polycrystalline standard. The incidence angle (0.1°) was slightly larger than the critical angle, ensuring that we sampled the full depth of the film. GIWAXS raw data was corrected for the geometric distortion introduced by a flat, plate detector, normalized by detector counts and film thickness, and reduced and analyzed using a combination of Nika 1D SAXS and WAXStools software packages in Igor Pro [9, 10]. Scattering data are presented in terms of scattering vector (denoted as Q or q)  $Q = 4\pi sin(\theta)/\lambda$ , where  $\theta$  is half the scattering angle and  $\lambda$  is the wavelength of incident X-rays. The terms  $Q_{xy}$  and  $Q_z$  denote the component of scattering vector in-plane and out-of-plane with the substrate, respectively. All X-ray measurements were performed in a Helium environment to minimize air scattering and beam damage to samples.

#### S1.4 Molecular Weight Characterization

The molecular weight distribution of the polymers was analyzed by matrix-assisted laser desorption/ionization timeof-flight (MALDI-TOF) mass spectrometry (Figure S4, Supporting Information) and gel permeation chromatography (GPC) in DMF. The MALDI-TOF measurements were carried out on a PerSeptive Biosystems (ABI)-Voyager-DE RP-MALDI-TOF mass spectrometer with DCTB as the matrix and measurements were conducted in positive mode. The GPC measurements were carried out on a Agilent Technologies 1260 infinity GPC in chloroform at 40  $^{\circ}$ C, using two PLgel 10 micrometer Mixed-B columns in series (300 × 7.5 mm), and calibrated against polystyrene standards (Đ< 1.10).

#### S1.5 Spectroelectrochemistry in reflection mode

A home-built spectrometer is employed to conduct the measurements using an Ocean Optics light source (Tungsten Halogen Light Sources) and detector (QEPro, Ocean Optics, 200  $\mu$ m slit width, cooled to -25 °C). A quartz cuvette (20mm optical path length) was equipped with a 3D printed substrate holder for polymer coated silicon substrates. A wire was soldered to the substrate and covered with epoxy glue. Spectroscopy measurements were carried out using an Ivium CompactStat potentiostat with an eDAQ leakless Ag/AgCl reference electrode and a Pt mesh counter electrode in Ar sat. 0.1 M NaCl aqueous electrolytes. Changes of the reflection spectrum are reported as a function of the applied potential when stepping the potential from -0.5 V to 0.5 V vs. Ag/AgCl with a step size of 0.1 V.

#### **S1.6** Bipotentiostat OECT Measurements

The in-situ conductivity test used for OECT measurements in this work was based on work by Kittelson et al. [11] and nomenclature for currents from Ref. [12]. Figure S1 shows a schematic of the experimental setup with relevant electronic currents labelled.



Figure S1: Bipotentiostat experimental setup for OECT device characterization. Reference (Ref or RE) counter (CE), and working (WE) electrodes are labelled, along with relevant current flows and definitions.

Applying Kirchoff's Rule to the device Source and Drain electrodes:

$$I_{1,m} = I_{1,cell} + I_{12} (S10)$$

and

$$I_{2,m} = I_{2,cell} - I_{12} \tag{S11}$$

If the polymer channel is uniform, covers each electrode equally, and has a relatively small Source-Drain voltage offset  $(V_{SD} \ll V_G)$ , then

$$I_{1,cell} \approx I_{2,cell} \tag{S12}$$

then:

$$I_{12} = \frac{I_{1,m} - I_{2,m}}{2} \tag{S13}$$

where  $I_{12}$  is the channel current, which can then be converted into film conductivity,  $\sigma$ , once film area and thickness is determined as shown in Equation S14.

$$\sigma = \frac{I_{12} \times Length}{V_{SD} \times Width \times Thickness}$$
(S14)

Furthermore, the current injected or collected from the film channel can be monitored accurately by the potentiostat readings of  $I_{1,cell} + I_{2,cell}$ , shown in Equation S15

$$Q = \int_{V_1}^{V_2} \frac{I_{1,cell} + I_{2,cell}}{\nu} dV$$
(S15)

where  $\nu$  is the voltage scan rate  $(V s^{-1})$  and Q is the injected charge (C). Equation S15 can be converted into charge density, n, with knowledge of the film volume. Finally, electronic carrier mobility,  $\mu$  can be found using the standard relation among charge density  $n (cm^{-3})$ , film conductivity  $\sigma (S cm^{-1})$ , and the fundamental charge e(C).

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$$\iota = \frac{\sigma}{n \, e} \tag{S16}$$

#### S1.7 Relative Conjugation Length Scaling

Relative conjugation length of H-aggregate type interacting units is calculated based on work by Barford [13] where it was shown that the conjugation length of interacting chromophores scales with the interchain exciton bandwidth (W) according to Equation S17:

$$W \sim L_{coni}^{-1.8} \tag{S17}$$

Where W is the exciton bandwidth as described in the Methods section and  $L_{conj}$  is the conjugation length of interacting chromophores. Because Equation S17 does not link W to  $L_{conj}$  absolutely, we use the *relative* conjugation length  $L_{conj,rel}$  as referenced to the conjugation length of p(g3T2) at -0.2V vs Ag/AgCl as shown in Equation S18:

$$L_{conj., rel.} = \frac{L_{conj., p(gXT2) @ Y V}}{L_{conj., p(g3T2) @ -0.2V}} = \left(\frac{W_{p(gXT2) @ Y V}}{W_{p(g3T2) @ -0.2V}}\right)^{\frac{-5}{9}}$$
(S18)

where  $L_{conj., p(gXT2) @ Y V}$  and  $W_{p(gXT2) @ Y V}$  represent the conjugation length and exciton bandwidth of p(g3T2) (X = 3) or p(g2T2) (X = 3) at a potential of Y V vs Ag/AgCl.

# S1.8 Ex-situ GIWAXS Stability analysis for p(g3T2) and discusion of backbone X-ray scattering peak

We use X-ray scattering peak breadth analysis to separate contributions of finite crystal size from the contributions of cumulative disorder to peak breadth. The peak breadth analysis is based on the work of Williamson and Hall, where the X-ray scattering peak breadth is given in Equation S19 [14, 15]

$$\Delta Q_{(h00)} = \frac{2\pi K}{L_{coh}} + \frac{\pi^2 g^2}{d_{(h00)}} h^2$$
(S19)

where  $\Delta Q_{(h00)}$  is the FWHM peak breadth as found from pseudo-voigt function fits to lamellar stacking peaks in our data, the (h00) family of peaks,  $L_{coh}$  is the coherence length of the (h00) planes, g is the paracrystallinity parameter,  $d_{(h00)}$  is the stacking distance of the (h00) planes (scattering peak at  $\approx 0.37$  Å<sup>-1</sup> gives a real space distance of 16.98 Å<sup>-1</sup>), h is the scattering peak order, and K is a shape factor, set to 0.9 in this study since the crystallite form is not well defined [15]. Equation S19 shows that a plot of  $\Delta Q_{(h00)}$  vs.  $h^2$  yields a line with slope  $m = \frac{\pi^2 g^2}{d_{(h00)}}$  and a y-intercept  $b = \frac{2\pi K}{L_{coh}}$ . We performed linear fits to the FWHM peak breadth of lamellar stacking peaks (the (h00) family of planes) in p(g3T2) after various ex-situ electrochemical charging experiments. The linear fit parameters (i.e. the Williamson-Hall type disorder fits) are shown in Table S3.

Figure S27 shows  $Q_{xy}$  lineouts and associated lattice spacings of the (001) peak in p(g3T2) after various ex-situ electrochemical charging experiments. Tracking the (001) peak, that is the "backbone" peak, in p(g3T2) after various ex-situ electrochemical cycling conditions shows that there is some structural disruption associated with ordering along the polymer backbone. This should not be interpreted as any changes to the monomer to monomer repeat distance, but instead likely represents subtle intermolecular slides and shifts of neighboring chains relative to each other, causing disruption in both the spacing associated with the (001) family of planes and the coherence of these planes.

# S2 Supplemental Figures

### S2.1 <sup>1</sup>H NMR spectra and Molecular Weight Characterization

For polymer p(g3T2), polymer chains with up to 30 repeat units are detected and GPC results show a number average molecular weight  $(M_n)$  of 23.9 kDa with a PDI of 2.42. The results are in agreement with previously reported findings [16] utilizing the same polymerization method. A lower molecular weight distribution was observed for p(g2T2) where polymer chains with fewer than 13 repeat units are detected from mass spectrometry. Results from GPC also indicate a lower molecular weight distribution of p(g2T2) with  $M_n$  of 8.5 kDa and a PDI of 2.94. The reason for the lower molecular weight distribution of p(g2T2) is most likely the lower solubility of the polymer that results in precipitation of the polymer during the polymerization.

### S2.2 <sup>1</sup>H NMR spectroscopy



Figure S2: NMR Spectrum of p(g2T2) in TCE-d<sub>2</sub>

<sup>1</sup>**H NMR (400 MHz, TCE-d**<sub>2</sub>)  $\delta$  6.98 (s, 2H), 4.37 (s, 4H), 3.99 (s, 4H), 3.83 (s, 4H), 3.65 (s, 4H), 3.42 (s, 6H); GPC (DMF, 40 °C)  $M_n = 8.5$  kDa,  $M_w = 25.1$  kDa.



Figure S3: NMR Spectrum p(g3T2) in CDCl<sub>3</sub>

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>)  $\delta$  6.99 (s, 2H), 4.38 (s, 4H), 4.03 – 3.95 (m, 4H), 3.85 – 3.80 (m, 4H), 3.76 – 3.70 (m, 4H), 3.70 – 3.64 (m, 4H), 3.56 – 3.51 (m, 4H), 3.37 (s, 6H); GPC (DMF, 80 °C)  $M_n$  = 23.9 kDa,  $M_w$  = 57.8 kDa.

### S2.3 MALDI-ToF measurements



Figure S4: Mass spectra of a) p(g2T2) and b) p(g3T2)

## S2.4 GPC analysis

The GPC measurements are carried out in DMF. We note that both polymers, p(g2T2) (and p(g3T2)), show strong bimodular elution in DMF. We assign this finding to the aggregate formation of polymers in DMF since the polymers have a lower solubility in DMF in comparison to chloroform to fabricate devices, the solvent used for processing the polymer. To avoid overestimation of the molecular weight measurements from GPC, we do not consider the high molecular weight fraction when calculating  $M_n$  and  $M_w$ .



Figure S5: GPC of p(g2T2) in DMF. a) GPC trace with polystyrene standard calibration and b) sample fraction with molecular weight calculation



Figure S6: GPC Trace of p(g3T2) in DMF. a) GPC trace with polystyrene standard calibration and b) sample fraction with molecular weight calculation

# S2.5 Spectroelectrochemical Characterization



Figure S7: As-cast and electrochemically discharged thin-film absorbance of p(g2T2) and p(g3T2). The discharged spectra were collected by applying -0.5V vs Ag/AgCl in 0.1 M NaCl aqueous electrolytes.



Figure S8: Differential absorption spectra for a) p(g3T2) and b) p(g2T2) normalized to the most maximum intensity in the range of 1.7-2.2 eV. Spectra are reported from charging potentials of -0.20 V to 0.5 V vs Ag/AgCl.



Figure S9: The intensity of certain absorbance features monitored during spectroelectrochemistry. Intensity of the maximum absorbance in the energy range of 1.8-2.1 eV as a function of a) film charging potential and b) electronic charge density, taken as a signature of uncharged aggregate backbone. The intensity of the maximum absorbance in the range of 1.35-1.5 eV as a function of c) film charging potential and d) electronic charge density taken as a signature of a polaronic absorption. In p(g3T2), polaron absorption is observed to decrease beyond 0.15 V vs Ag/AgCl, and we take this as a sign that bipolaron absorption is starting to increase.



Figure S10: Model fits to differential absorption spectra of p(g3T2) based on Equations S2 and S5. Experimental data are shown as symbols, the total model fit is shown as red solid lines, and the individual vibronic components of the fit (e.g. 0-0 transition, 0-1 transition, etc.) are shown as dashed lines. Data are from 50 mV steps around a) -0.20, b) -0.15, c) -0.10, d) -0.05, e) 0, f) 0.05, g) 0.10 and h) 0.15 V vs Ag/AgCl.



Figure S11: Model fits to differential absorption spectra of p(g2T2) based on Equations S2 and S5. Experimental data are shown as symbols, the total model fit is shown as red solid lines, and the individual vibronic components of the fit (e.g. 0-0 transition, 0-1 transition, etc.) are shown as dashed lines. Data are from 50 mV steps around a) -0.20, b) -0.15, c) -0.10, d) -0.05, e) 0, f) 0.05, g) 0.10, h) 0.15, and i) 0.20 V vs Ag/AgCl.



Figure S12: Integrated aggregate absorption cross section as found from vibronic fitting of spectroelectrochemical differential absorbance data (Figures S10 and S11) for p(g3T2) and p(g2T2) as a function of a) potential [V vs Ag/AgCl] and b) charge carrier density. This effectively tracks the amount of aggregates by spectral integration of the model fits shown in Figures S10 and S11 that are charged at each potential step.



Figure S13: Top row, interchain exciton bandwidth as determined from vibronic model fits to spectroelectrochemistry differential absorbance of p(g3T2) and p(g2T2) and bottom row, the relative conjugation length ( $L_{conj., rel.}$ ) of bleached backbone aggregates as calculated from the exciton bandwidth via the relation shown in Equation S18 as a) functions of potential [V vs. Ag/AgCl] and b) as functions of charge carrier density found from integrating the CV traces shown in Figure 3a.

### S2.6 Electrochemical characterization and electronic transport properties

Polymer	E <sub>1/2</sub> [1] [V vs Peak differential		Peak total mobility	Charge density at peak differential	
	Ag/AgCl]	mobility $[cm^2V^{-1}s^{-1}]$	$[cm^2V^{-1}s^{-1}]$	mobility $[10^{20} cm^{-3}]$	
p(g2T2)	0.4	0.009	0.004	5.9	
p(g3T2)	-0.1	0.26	0.10	2.4	

Table S2: OECT Transport Properties of the polymers p(g2T2) and p(g3T2)



Figure S14: CV measurements of polymer thin films between -0.5 V to 0.5 V vs. Ag/AgCl for a) p(g2T2) and b) p(g3T2) and between -0.5 V to 0.8 V vs. Ag/AgCl for c) p(g2T2) and d) p(g3T2). All measurements were carried out with a scan rate of 50 mV/s. The highlighted areas in c) and d) show irreversible electrochemical redox-reactions of the polymers.



Figure S15: Role of the substrate on the electrochemical redox-potentials of the polymers in aqueous electrolytes. A shift of the oxidation onset for p(g2T2) and p(g3T2) is observed when ITO coated glass substrates or p++ silicon substrates substrates are used a,b) cyclic voltammograms, c) changes of the absorption spectrum (at  $\lambda_{max}$ ) and d) changes of the reflection spectrum (at  $\lambda_{max}$ ).



Figure S16: Electrochemical characterization of p(g2T2) on p++-doped silicon substrates. a) CV measurements between -0.5 V to 0.5 V vs. Ag/AgCl with a scan rate of 50 mV/s (device area is 1.54 cm2, thickness: 110 nm) in 0.1 M NaCl aqueous electrolyte with low O2 concentration. b) Picture of the device, and c) CA measurements, applying the indicated potential for 5 minutes, followed by monitoring the OCV (dashed line). The red curve represents the charge injected/collected for each experiment, an increase in the injected charge is indicative of electrochemical side reactions with the electrolyte.



Figure S17: Electrochemical characterization of p(g3T2) on p++-doped silicon substrates. a) CV measurements between -0.5 V to 0.5 V vs. Ag/AgCl with a scan rate of 50 mV s<sup>-1</sup> (device area is 1.92 cm<sup>2</sup>, thickness: 230 nm) in 0.1 M NaCl aqueous electrolyte with low O2 concentration. b) Picture of the device, and c) CA measurements, applying the indicated potential for 5 minutes, followed by monitoring of the OCV (dashed line). The red curve represents the charge injected/collected for each experiment, an increase in the injected charge is indicative of electrochemical side reactions with the electrolyte.



Figure S18: OECT measurements (50  $\mu$ m channel) of p(g2T2) and p(g3T2) in 0.1 M NaCl in Ar sat. solution, with V<sub>D</sub> = 10 mV and a scan rate of 100 mV s<sup>-1</sup>. a) Cyclic voltammogram of the polymers (scan #1-5), b) correlation between the potential (vs. Ag/AgCl) and the charge carrier density, c) correlation between the electronic conductivity as a function of the charge carrier density and d) calculated differential mobility and normalized transconductance with respect to the charge carrier density. The channel dimensions of the devices are: W = 2 mm,  $L = 50 \mu \text{m}$  with d = 199 nm for p(g2T2) and 149 nm for p(g3T2).



Figure S19: OECT measurements of p(g2T2) in Ar sat. 0.1 M NaCl solution, with  $V_D = 10$  mV and scan rates of 25-200 mV s<sup>-1</sup>. a) Current density (charging cycle) and b) correlation between charge carrier density and potential (vs. Ag/AgCl), c) electronic conductivity as a function of the charge carrier density and d) calculated differential mobility  $(\partial d\mu = \frac{d\sigma}{dn}e)$  with respect to charge carrier density. The channel dimensions of the devices are: W = 2 mm, L = 100  $\mu$ m with an average d of 199 nm for p(g2T2).



Figure S20: OECT measurements of p(g3T2) in Ar sat. 0.1 M NaCl solution, with  $V_D = 10$  mV and scan rates of 25-200 mV s<sup>-1</sup>. a) Current density (charging cycle) and b) correlation between charge carrier density and potential (vs. Ag/AgCl), c) electronic conductivity as a function of the charge carrier density and d) calculated differential mobility  $(\partial d\mu = \frac{d\sigma}{dn}e)$  with respect to charge carrier density. The channel dimensions of the devices are: W = 2 mm, L = 100  $\mu$ m with an average d of 149 nm for p(g3T2).



Figure S21: Stability of p(g2T2) when operated at potentials of 0.5 V or 0.8 V vs. Ag/AgCl [V]( $V_D = 10 \text{ mV}$  at a scan rate of 5 mV s<sup>-1</sup>) in Ar. sat.0.1 M NaCl solution: Current density when charged to a) 500 mV and d) 800 mV, showing scan # 1-5 (the arrow indicates the difference of the conductivity between scan #1 and #5), conductivity (Scan # 1-5) when charged to b) 500 mV and e) 800 mV and differential (solid blue line), total mobility (dashed blue line) and normalized transconductance (yellow solid line) when charged to c) 500 mV and f) 800 mV (showing scan #1, forward). The channel dimension of the device is: W = 2 mm,  $L = 100 \mu \text{m}$  with an average d of 199 nm.



Figure S22: Stability of p(g3T2) when operated at potentials of 0.3 V or 0.5 V vs. Ag/AgCl [V] ( $V_D = 10 \text{ mV}$  at a scan rate of 100 mV s<sup>-1</sup>) in Ar. sat.0.1 M NaCl solution: Current density when charged to a) 300 mV and d) 500 mV) showing Scan # 1-5, conductivity (Scan # 1-5) when charged to b) 300 mV and e) 500 mV and differential (solid blue line), total mobility (dashed blue line) and normalized transconductance (yellow solid line) when charged to c) 300 mV and f) 500 mV, showing scan #1, forward. The channel dimension of the device is: W = 2 mm,  $L = 100 \mu \text{m}$  with an average *d* of 149 nm.



Figure S23: Comparison of the OECT performance of p(g3T2) in Ar sat. 0.1 M NaCl solution (with  $V_D = 10 \text{ mV}$  with a scan rate of 100 mV s<sup>-1</sup>) when cycled between -500 mV and +300 mV or +500 mV. a) current density during charging and discharging (Scan # 1-5), b) conductivity (Scan # 1-5) and c) differential mobility (total mobility is shown as a dashed line). The channel dimensions of the devices are: W = 2 mm,  $L = 100 \mu \text{m}$  with an average d of 149 nm.

### S2.7 GIWAXS Characterization



Figure S24: 2D GIWAXS patterns of a p(g2T2) film measured immediately after ex-situ charging to various applied potentials with 0.1 M NaCl. Numbers in parenthesis denote the charging step.



Figure S25: In-plane  $(Q_{xy})$  and out-of-plane  $(Q_z)$  X-ray scattering lineouts of a p(g2T2) film ex-situ charged with 0.1 M NaCl to various charged potentials. Lineouts have been vertically offset to accentuate the peak shifts.



Figure S26: 2D GIWAXS patterns of a p(g3T2) film measured immediately after ex-situ charging to various applied potentials with 0.1 M NaCl. Numbers in parenthesis denote the charging step. Note, lineouts for p(g3T2) are shown in the main text Figure 5.



Figure S27: a)  $Q_{xy}$  lineouts of the (001) peak for p(g3T2) and b) (001) peak spacing as found from pseudo-voigt function fits to the  $Q_{xy}$  lineouts at various swelling/charging conditions. ex-situ GIWAXS data was collected at charging steps of 0.2 V vs Ag/AgCl for the first charging cycle, and the subsequently, data was only collected for the nominally reduced polymer charged to -0.4 V vs Ag/AgCl after 2 and 50 charging cycles where the polymer charged following the same charging steps outlined in Figure 5.

Condition	b [Å <sup>-1</sup> ]	m [Å <sup>-1</sup> ]	$L_{coh,(h00)} [Å^{-1}]$	g [%]	~rDoC [fr.]
initial	$0.044 \pm 0.003$	$0.0052 \pm 0.0005$	134.4	9.4	1.00
Stress Cycle 2	$0.053 \pm 0.005$	$0.0063 \pm 0.0005$	111.7	10.4	0.87
Stress Cycle 50	$0.066 \pm 0.004$	$0.0076 \pm 0.0008$	89.6	11.4	0.52

### S2.8 Properties of Low Molecular Weight p(g3T2)

To account for possible structural and redox-behavior differences originating from variations in the molecular weight of the polymers, we synthesized a polymer batch of p(g3T2) with a lower molecular weight distribution ( $M_n$  of 10.3 kDa and a D of 2.2, see Table S4) and comparable repeat units as observed for polymer p(g2T2). While both batches of p(g3T2) exhibit similar redox-behavior and solid-state morphology, we observed faster delamination during the charging of polymer thin films with the lower molecular weight batch of p(g3T2). We hypothesize that the lower stability of the devices originates from the expected decrease in mechanical properties for polymers with lower molecular weight distributions [17], in particular when charging the polymer in aqueous electrolytes where a large degree of swelling was reported for p(g3T2) [18, 19]. In the present work, we thus focus on studying the higher molecular weight batch of p(g3T2). Film mechanical instability prevented a full comparison of electronic transport properties of the low molecular weight p(g3T2) on electronic transport cannot be excluded. Nevertheless, we emphasize that the solid-state microstructure, CV properties, photophysical properties under electrochemical charging (see S32), and aggregate fraction of the low molecular weight p(g3T2) are remarkably similar to that of the higher molecular weight p(g3T2), emphasizing that many of the observed differences between p(g3T2) and p(g2T2) are a result of the different side chain lengths and not molecular weight.

Table S4: Properties Low Molecular Weight p(g3T2)

Polymer	M <sub>n</sub> [kDa]	E <sub>Ox</sub> [V vs Ag/AgCl]	<i>W</i> [meV]	Aggregate Amount [%]	Lamellar Spacing [nm] / Coherence Length [nm]
p(g3T2)-Low	10.3 / 2.2	-0.2	$78 \pm 8$	48 ± 6	1.70 / 12.2



Figure S28: CV of low molecular weight p(g3T2) over three charging/discharging cycles.



Figure S29: UV-Vis spectrum of discharged, neutral polymer thin film of low molecular weight p(g3T2) with fits of vibronic model described in Ref. [1]. Experimental data is shown as symbols, the model fit is shown as a solid line, and the individual vibronic components of the model fit are shown as dashed lines. Using Equation S2 and  $\lambda^2 = 0.95$ , exciton bandwidth was found  $W = 78 \pm 8$  meV and the fraction of aggregates was found to be  $48 \pm 6\%$ .



Figure S30: 2D GIWAXS patterns of a low molecular weight p(g3T2) in the as-cast state. Qualitatively more isotropic lamellar and  $\pi$ -stacking orientation is observed in the low molecular weight p(g3T2) than that observed in the high molecular weight p(g3T2) shown in Figure S26



Figure S31: a) In-plane (Qxy) and b) out-of-plane (Qz) X-ray scattering lineouts of a low molecular weight p(g3T2) and high molecular weight p(g3T2). Scattering lineouts have been vertically offset for clarity. There is a peak of unconfirmed origin at  $Qz \sim 0.9 \text{ Å}^{-1}$ . The lamellar stacking distance is 1.70 nm with an estimated lamellar coherence of 12.4 nm



Figure S32: Ratio of 0-0 and 0-1 vibronic absorption features ( $R_{00/01}$ ), W, and fraction of injected holes going to aggregates (Fractional Agg. Charging) as found from vibronic model fits to differential UV-Vis absorption of p(g3T2), p(g2T2) and low molecular weight p(g3T2) (p(g3T2)-low in the figure).  $R_{00/01}$  values above unity are highlighted in gray.

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