Supporting Information

Diverse Synaptic Plasticity Induced by the Interplay of Ionic Polarization and Doping at Salt-Doped Electrolyte/Semiconducting Polymer Interface

Yuandong Hu,†,‡ Fei Zeng,*,†,‡,§ Chiating Chang,†,‡ Wenshuai Dong,†,‡ Xiaojun Li,†,‡ Feng Pan,*† and Guoqi Li‡

†Laboratory of Advanced Materials (MOE), School of Materials Science and Engineering, and ‡Center for Brain Inspired Computing Research (CBICR), Tsinghua University, Beijing 100084, People’s Republic of China

§Key Laboratory of Microelectronic Devices & Integrated Technology, Institute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, People’s Republic of China

*Correspondence to: Fei Zeng (E-mail: zengfei@mail.tsinghua.edu.cn, panf@mail.tsinghua.edu.cn)
1. Structure of PEO, P3HT and PEO/P3HT films

![XRD spectra of the films.](image)

**Figure S1.** XRD spectra of the films.

Previous studies confirmed the ionic conductivity of salt dissolved PEO strongly depended on phase segregation, which led to a crystalline phase of PEO, a crystalline phase of PEO-salt complex, and an amorphous phase. Among them, the amorphous phase is the primary contributor of ionic conductivity. To explore the crystallization of PEO-Ca$^{2+}$ electrolyte, the XRD patterns were obtained and shown in Figure S1. In the range of 20 from 15° to 25°, the P3HT film exhibited no characteristic peaks. In comparison between PEO-Ca$^{2+}$ single layer and PEO-Ca$^{2+}$/P3HT double layer with EO:Ca$^{2+} = 32:1$, the typical peaks of crystallized PEO at about 19.2° and 23.3° were found in both samples, showing the consistent crystallization sate for PEO-Ca$^{2+}$ complex on Pt-coated substrate and P3HT coated substrate. The XRD pattern of the
sample with EO:Ca$^{2+}$ = 16:1 exhibited another diffraction peak at 16.9°, which represented the crystalline PEO-salt complex.$^3$ The peaks of Ca(CF$_3$SO$_3$)$_2$ were not observed in all samples containing PEO, indicating the salt was fully dissolved into PEO or negligible Ca(CF$_3$SO$_3$)$_2$ salt. Thus, we could conclude that in the P3HT/PEO-Ca$^{2+}$ (EO:Ca$^{2+}$ = 32:1) device, the electrolyte consisted of the crystallized PEO phase and the amorphous phase, and Ca$^{2+}$ transport channels mainly existed in amorphous region which was surrounded by crystalline lamellae.$^{4-5}$

Figure S2. XRD spectra of P3HT films with different annealing process

In Figure S2, we show the XRD pattern of P3HT film on Pt/Si substrate with different annealing process. In the range of 2θ from 4° to 10°, the Pt/Si substrate showed no peaks, and the typical diffraction peaks of crystalline P3HT at 5.4° were found in all P3HT samples. The characteristic peaks of samples with complete annealing (at 100 °C for 1 h and then at 120 °C for 20 min, or at 100 °C for 12 h) exhibited larger intensity than those with incomplete annealing (at 100 °C for 1 h, or at 50 °C for 1 h, or without annealing), suggesting better crystallization of P3HT with annealing under higher temperature or longer time. The previous study showed the characteristic peaks at about 5.4° and 23.4° respectively corresponded to edge-on and face-on chain orientation under out-of-plane measurement.$^6$ As the peak at 5.4° was
found (in Figure S2 deep blue line) and the peak at 23.4° was not found (in Figure S1), we can conclude that the P3HT film we used in synaptic experiments (annealed at 100 °C for 1 h and then at 120 °C for 20 min) displayed edge-on stacking mode of P3HT chains. This molecular alignment has been thought to hinder charge transfer across the molecule/metal interface. We think it might result in the difficulty for ionic doping into the P3HT layer as shown in the following Raman spectra of the initial state (Figure S3) and short term plasticity in Figure 2.

![Raman spectra of P3HT and P3HT/Ca-Tf₂ mixture films.](image)

**Figure S3.** Raman spectra of P3HT and P3HT/Ca-Tf₂ mixture films. For the mixture, the ratios of P3HT/ Ca-Tf₂ are 40:1, 40:5 and 40:25, respectively. The solution is 1,2-dichlorobenzene.
In situ Raman analysis has found that ionic doping into P3HT occurred under the external bias.\textsuperscript{8-9} Our previous study has found that the initial state of P3HT was not doped for the salt-doped PEO/P3HT double layer.\textsuperscript{10} We further mixed P3HT and Ca-PEO, and found that the main peak (1445 cm\textsuperscript{-1}) and the second strong peak (1378 cm\textsuperscript{-1}) are not moved, and the relative strength is not changed (Figure S3) yet. However, we found that the ratio of integration for these two peaks was enlarged compared with pure P3HT. For example, the ratio was 7.96 for the pure P3HT but 9.22 for the sample of PEO-CaTf\textsubscript{2} (40:1), 11.3 for the sample of PEO-CaTf\textsubscript{2} (40:5). The broadness of the main peak might relate to the reduction of the molecule domain for P3HT, which might enhance the diffusion probability of ions through the intervals into the molecule rings. This suppose needs in situ monitoring under the condition of applying bias.

2. Electrical properties of PEO-Ca(CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} single layer, P3HT single layer and PEO/P3HT double layer
**Figure S4.** I-V curves of PEO-Ca(CF₃SO₃)₂ single layer sample under voltage sweeping rate of 100 V/s. Curves of (a) positive and (b) negative voltage sweeping were basically symmetric, and no NDR effect appeared when applied by positive bias.

The direct current property of PEO complex single layer device (EO:Ca=32:1) was measured under voltage sweeping rate of 100 V/s as shown in Figure S4. The I-V curves exhibited obvious hysteresis loop, which corresponded to ionic migration and formation of dielectric double layer under bias. Unlike rectification property of PEO-Ca(CF₃SO₃)₂/P3HT double layer devices (shown in Figure 1), single layer device showed nearly symmetric I-V curves when swept form 0-2 V and 0-(2) V. It indicated that by introducing a semiconducting polymer layer, the migration of cations is clearly blocked when applied positive bias.¹⁻³ We did all electrical experiment at the room temperature. The ionic conductivity of PEO-salt complex will significantly decreased as temperature drops, and when temperature rises, PEO may turn to viscous state, which is to the disadvantage of application.¹⁻³

**Figure S5.** I-V property of P3HT Film
The conduction of the P3HT film was examined as shown in Figure S5. One can see that the Pt film was about 33.5 $\Omega$ when the two probes were in the distance of 2 mm. The resistance of P3HT film is that perpendicular to the film plane and about 30 $\Omega$. This value demonstrates that the resistance of P3HT film contribute less to that of the PEO-Ca(CF$_3$SO$_3$)$_2$/P3HT double layer and the interface polarization is the origin of the enhanced resistance and rectification.

![Nyquist Impedance Spectra](image)

**Figure S6.** (a) Nyquist impedance spectra of PEO-Ca$^{2+}$ single layer device from 1 kHz to 1 MHz. Fit parameters are $R_{\text{ion}} = 1.030E+07 \Omega$, $Q_{\text{int}} = 8.120E-09 \text{ F} \cdot \text{s}^{-1}$, $a_{\text{int}} = 0.85$, $Q_{\text{bulk}} = 1.995E-11$ and $a_{\text{bulk}} = 1$. (b) Nyquist impedance spectra of P3HT/PEO-Ca$^{2+}$ double layer device from 1 kHz to 1 MHz. Fit parameters are $R_{\text{ion}} = 2.206E+06 \Omega$, $Q_{\text{int}} = 1.716E-08 \text{ F} \cdot \text{s}^{-1}$, $a_{\text{int}} = 0.267$, $Q_{\text{bulk}} = 3.462E-12$ and $a_{\text{bulk}} = 0.985$. The hollow spots correspond to measured data, and the red curves correspond to the fit results using the equivalent circuits in the inset.

In Figure S6, we show the Nyquist impedance of PEO-Ca$^{2+}$ single layer device (EO:Ca=32:1). As the ionic migration dominated the charge transportation, the impedance spectra supposed to be a single semicircle at high frequency and a capacitive
tail at low frequency. Since the low-frequency signal of thin-film device was quite
instable due to the great roughness of PEO, the frequency range started from 1 kHz to 1
MHz, resulting in the loss of the capacitive tail. An equivalent circuit shown in the inset
of Figure S6a was built according to the reported method.\textsuperscript{11} We chose a cylinder with
100 μm radius (the same as the island electrode) and 20 μm height (the same as the
thickness of PEO-Ca\textsuperscript{2+} layer) as a simplified geometry of the sandwiched device, then
obtained the ionic conductivity of 6.18E-7 S/cm in single layer device, which was
within the range of reported conductivity value of PEO+salt complex.\textsuperscript{1,3} In Figure S6b
we show the Nyquist impedance of PEO-Ca\textsuperscript{2+}/P3HT double layer device (EO:Ca=32:1).
The standard analysis using the same equivalent circuit showed a less obvious
semicircle at high frequency, which indicated the significantly modulation of ion
migration by PEO/P3HT interface.

3. Pulse responses of the Ca\textsuperscript{2+}-PEO single layer device

We examined pulse responses of the Ca\textsuperscript{2+}-PEO single layer device as shown in Figure
S7. The pulse sequences were composed of 200 triangular pulses with amplitude of 0.7
V and loading rate of 100 V/s. The discharging peaks were adopted as well as that
described in the main text as post-spike current (PSC) for weight calculation. As pulse
number and frequency increases, the responding current monotonically increased, which
resembles a merely facilitating short-term plasticity. We attributed this capacitor-like
property to accumulation of ions at both side of the salt-doped PEO electrolyte, and
established a quantitative model to describe the contribution of this process to internal
electrical field. Comparing to double layer device, the lack of depression at a time scale of a few seconds indicated that there was no physical or chemical process that interfered the internal field.

Figure S7. (a) Pulse response of PEO-Ca(CF$_3$SO$_3$)$_2$ single layer device varies with pulse number. (b) Weight modification varied with frequency. The curve showed monotonically increasing characteristic with frequency of pulses increases.

4. The fit curves and the values of the parameters for the pulse responses of PEO-Ca(CF$_3$SO$_3$)$_2$/P3HT double layer device.

Figure S8 shows the experiment data (hollow spots) and the simulating results (red lines) for the device with EO:Ca$^{2+}$ ratio of 32:1. Apparently, the model based on
facilitation component ($F$) and depression component ($D$) accurately fits the diverse plasticity of the device.

In the simulation, parameters were device-specific, which means all of them should have been fixed in different frequency tests. However, when we fixed the value of $\tau_F$, $\tau_D$, $\alpha$ and $\beta$ in the simulation, the value of $f$ quickly stabled when frequency increased, but the value of $d$ decreased meanwhile, as shown in Tab. S1. We attribute this to the dependence of $d$ on facilitation component $F$, i.e. the level of electrochemical doping during each pulse relates to concentration of ions accumulated at PEO/P3HT interface.
**Figure S8.** The experiment data (hollow spots) and the simulating results (red lines) of the devices with EO:Ca$^{2+}$ ratio of 32:1 in different frequency tests. (a)–(h) correspond to 10 Hz, 20 Hz, 40 Hz, 50 Hz, 66.7 Hz, 80 Hz, 100 Hz, 125 Hz test respectively.

**Table S1.** The value of parameters used in the simulations of the devices with EO:Ca$^{2+}$ ratio of 32:1.

|       | 10 Hz  | 20 Hz  | 40 Hz  | 50 Hz  | 66.7 Hz | 80 Hz  | 100 Hz | 125 Hz |
|-------|--------|--------|--------|--------|---------|--------|--------|--------|
| $\tau_F$ | 0.0115 |        |        |        |         |        |        |        |
| $\alpha$ | 0.5159 |        |        |        |         |        |        |        |
| $\tau_D$ |        | 2.2632 |        |        |         |        |        |        |
| $\beta$ |        | 1      |        |        |         |        |        |        |
| $f$   |        | 0.42517| 0.18882| 0.16971| 0.19627| 0.19941| 0.18695| 0.20866|
| $a$   | -      | 0.01223| 0.10769| 0.16641| 0.25736| 0.31964| 0.39733| 0.47288|
| $d$   | 8.72E-04| 7.96E-04| 6.49E-04| 5.28E-04| 4.23E-04| 3.36E-04| 2.06E-04| 1.07E-04|
| $b$   | 0.95974| 0.98118| 0.99208| 0.99427| 0.99648| 0.99757| 0.99868| 0.99956|

These value derived from least square fitting of 200 experiment data points by Equation (14). The value of $a$ and $b$ can be deduced from $\tau_F$, $\tau_D$, $\alpha$, $\beta$ and the pulse interval $\Delta t$ according to Equation (10). The value of $f$ and $a$ in 10 Hz experiment cannot be got because the facilitation period is indiscernible.

5. **Simulation parameters of the post-tetanic stimulation experiment.**

As we discussed in the paper, the post-tetanic plasticity also fits our model. The device was stimulated by a complex train of pulses (triangular pulses with amplitude of 0.7 V and loading rate of 100 V/s) consisting of 1 Hz (20 pulses)-high frequency (200 pulses)-1 Hz (20 pulses). As $\tau_F$ was far smaller than $\tau_D$ in our model, depression
dominated the post-tetanic stimulation. According to Equation (20), we fit experiment data using parameters as shown in Table S2.

**Table S2.** The value of parameters \((d, b, p)\) in Equation (17). These value derived from least square fitting of 20 experiment data points of 1 Hz stimulation after tetanus stimuli.

|          | 20 Hz  | 40 Hz  | 50 Hz  | 66.7 Hz | 80 Hz  | 100 Hz |
|----------|--------|--------|--------|---------|--------|--------|
| \(d\)    | 0.97223| 0.93918| 0.92896| 0.90167 | 0.8999 | 0.88787|
| \(b\)    | 0.48993| 0.47073| 0.50247| 0.52945 | 0.52505| 0.5224 |
| \(p\)    | -0.01222| -0.03057| -0.03422| -0.04627| -0.04739| -0.0541|

REFERENCES

1. Marzantowicz, M.; Dygas, J. R.; Krok, F.; Lasinska, A.; Florjanczyk, Z.; Zygadlo-Monikowska, E.; Affek, A., Crystallization and melting of PEO : LiTFST polymer electrolytes investigated simultaneously by impedance spectroscopy and polarizing microscopy. *Electrochim Acta* 2005, 50, 3969.
2. Marzantowicz, M.; Dygas, J. R.; Krok, F.; Nowinski, J. L.; Tomaszewska, A.; Florjanczyk, Z.; Zygadlo-Monikowska, E., Crystalline phases, morphology and conductivity of PEO : LiTFSI electrolytes in the eutectic region. *J. Power Sources* 2006, 159, 420.
3. Mehta, M. A.; Lightfoot, P.; Bruce, P. G., Phase-Diagram of The Poly(Ethylene Oxide)Ca(CF3so3)2 System. *Chem. Mater.* 1993, 5, 1338.
4. Cheng, S.; Smith, D. M.; Li, C. Y., How Does Nanoscale Crystalline Structure Affect Ion Transport in Solid Polymer Electrolytes? *Macromolecules* 2014, 47, 3978-3986.
5. Young, W. S.; Brigandi, P. J.; Epps, T. H., Crystallization-Induced Lamellar-to-Lamellar Thermal Transition in Salt-Containing Block Copolymer Electrolytes. *Macromolecules* 2008, 41, 6276–6279.
6. Aryal, M.; Trivedi, K.; Hu, W. W., Nano-Confinement Induced Chain Alignment in Ordered P3HT Nanostructures Defined by Nanoimprint Lithography. *ACS NANO* 2009, 3, 3085-3090.
7. Maia, F. C. B.; Miranda, P. B., Molecular Ordering of Conjugated Polymers at Metallic Interfaces Probed by SFG Vibrational Spectroscopy. *J. Phys. Chem. C* 2015, 119, 7386-7399.
8. Shoute, L. C. T.; Pekas, N.; Wu, Y. L.; McCreery, R. L., Redox driven conductance changes for resistive memory. *Appl Phys A* **2011**, *102*, 841-850.

9. Rajesh Kumar, R.; Pillai, R. G.; Pekas, N.; Wu, Y. L.; McCreery, R. L., Spatially Resolved Raman Spectroelectrochemistry of Solid-State Polythiophene/Viologen Memory Devices. *J. Am. Chem. Soc.* **2012**, *134*, 14869 - 14876.

10. Zeng, F.; Lu, S. H.; Li, S. Z.; Li, X. J.; Pan, F., Frequency Selectivity in Pulse Responses of Pt/Poly(3-Hexylthiophene-2,5-Diyl)/Polyethylene Oxide + Li⁺/Pt Hetero-Junction. *PLoS ONE* **2014**, *9*, e108316.

11. Patel, S. N.; Javier, A. E.; Stone, G. M.; Mullin, S. A.; Balsara, N. P., Simultaneous Conduction of Electronic Charge and Lithium Ions in Block Copolymers. *ACS Nano* **2012**, *6*, 1589–1600.

12. Liu, A.; Zeng, F.; Hu, Y. D.; Lu, S. H.; Dong, W. S.; Li, X. J.; Chang, C. T.; Guo, D., Simulation of pulse responses of lithium salt-doped poly ethyleneoxide. *J. Polym. Sci., Part B: Polym. Phys.* **2016**, *54*, 831–837.