Supplementary Information

Mixed Binary Supporting Electrolyte Approach for Enhanced Synaptic Functionality in One-shot Integrable Electropolymerized Synaptic Transistors

Jiyun Lee,[a,1] Jaehoon Lee,[a,1] Hyeonsu Bang,[b] Tae Woong Yoon,[a] Jong Hwan Ko,[c] Boseok Kang[a,d,*]

*Corresponding author: bskang88@skku.edu (Prof. B. Kang)

[a]SKKU Advanced Institute of Nanotechnology (SAINT) and Department of Nano Science and Technology, Sungkyunkwan University,
2066 Seobu-ro, Jangan-gu, Suwon 16419, Korea

[b]Department of Electrical and Computer Engineering, Sungkyunkwan University
2066 Seobu-ro, Jangan-gu, Suwon, 16419, Korea

[c]College of Information and Communication Engineering, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon 16419, Republic of Korea

[d]Department of and Nano Engineering and Semiconductor Convergence Engineering, Sungkyunkwan University
2066 Seobu-ro, Jangan-gu, Suwon, 16419, Korea

Keywords: Mixed binary supporting electrolyte, ADC bipolar electropolymerization, one-shot integrable electropolymerization, conductive polymers, organic electrochemical synaptic transistors

Materials

3,4-ethylenedioxythiophene (EDOT, 99%) and acetonitrile (MeCN, HPLC grade) were purchased from Thermo Fisher Scientific Co. and J.T. Baker Chemical Co., respectively. *p*-Benzoquinone (BQ, 99.5%), tetrabutylammonium tetrafluoroborate ($TBABF_4$, 99%), 1-ethyl-3-methylimidazolium biis(trifluoromethylsulfonyl)imide (EMIM:TFSI, 98%), poly(ethylene glycol) diacrylate (PEGDA), and 2-hydroxy-2-methylpropiophenon (HOMPP, 97%) were purchased from Sigma-Aldrich Co. All the chemicals were used as received without further purification.

Preparation of one-shot integrable electropolymerized (OSIEPed) films

(i) BPE array-patterned substrate

Soda glass substrates (20 × 20 mm^2) were prepared by sequential washing in acetone, isopropyl alcohol, and deionized water for 15 min each, followed by drying under a nitrogen (N_2) stream. The BPE array-patterned substrate was prepared via the thermal deposition of Ti (4 nm) and Au (25 nm) layers using a shadow mask.

(ii) Reactive solution preparation

The reactive solution was prepared by dissolving 3 mM EDOT, 3 mM BQ, and 1.5 mM supporting electrolyte in MeCN. A fresh reactive solution was prepared immediately before OSIEP, and 10 mL of the solution was used for each batch.

(iii) OSIEP process

The OSIEP process was carried out using an AC/DC power source (EC1000SA, NF Corporation) in accordance with the method described in literature. The seeding step for the three PEDOT:anion films was conducted for 3 s at 35 V_{rms} of V_{AC} with a frequency of 3 Hz, followed by 3 s at 40 V_{rms} with the same frequency. During the propagation step, a voltage combining V_{AC} and V_{DC} (40 V_{rms} at 3 Hz and 1 V, respectively) was applied. The OSIEP times were 2 min for PEDOT:BF_4, 2.75 min for PEDOT:Blend, and 4.5 min for PEDOT:TFSI for the overall step.

(iv) Fabrication of organic electrochemical synaptic transistors

The gate electrolyte was patterned using a nozzle dispenser (350 PC, Musashi Engineering, Inc.) to fabricate a three-terminal organic electrochemical transistor-based synaptic device. The uncured ion gel was composed of PEGDA, HOMPP, and EMIM:TFSI at a weight ratio of 2:1:21. The synaptic characteristics were evaluated after curing the patterned ion gel under 354 nm UV light.

Computational method

Density functional theory calculations were carried out at the B3LYP level with the 6-31+G(d,p) basis set without applying basis set superposition error correction. $E_{int.}$s was determined by calculating the total energy of the interacting molecular system ($E_{A\text{-}B}$) and subtracting the optimized energies of the individual molecules ($E_{A,opt}$ and $E_{B,opt}$) using $E_{int.} = E_{A\text{-}B} - E_{A,\,opt} - E_{B,\,opt}$. To analyze interactions between the PEDOT backbone and the counter anions (BF_4^- or $TFSI^-$), molecular models were constructed, each comprising EDOT trimer units with a single positive charge (tri-$EDOT^+$) paired with the corresponding counter anions.

Characterization

Structural and spectroscopic analyses were performed on the as-fabricated PEDOT:anion films. High-resolution images were obtained using field-emission SEM (S-5200, Hitachi). The thickness, topographic information, and surface energy were obtained using atomic force microscopy (AFM, NX10, Park Systems). Surface potential variations of the Φ_{film} were measured by KPFM, which is an AFM-based technique done by measuring the contact potential difference. A map of the contact potential difference, or the surface potential of a sample relative to that of a biased tip (NSC36/Cr-Au), was calibrated before and after every measurement using highly ordered pyrolytic graphite, with a well-established work function of 4.6 eV. The real Φ_{film} values of the three OSIEPed films were calculated from the measured surface potential of each sample, with respect to the tip work function ($\Phi_{film} = \Phi_{tip} - eV$). The UV-Vis-NIR absorbance spectra were recorded using a UV-Vis-NIR spectrophotometer (V-770, JASCO). GIWAXS measurements were performed on the 3C beamline of the Pohang Accelerator Laboratory, Republic of Korea. Electrical characterization of the synaptic transistors was conducted using the Keithley 4200-SCS and Keithley 2636A Sourcemeter unit under vacuum ($P \approx 10^{-6}$ Torr).

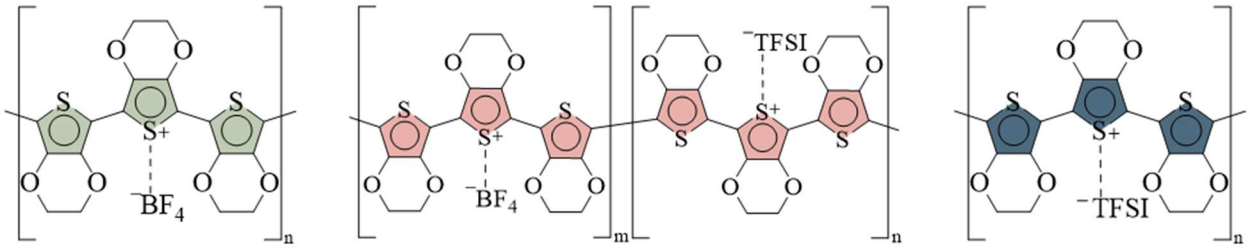

Fig. S1 Molecular structures of the three OSIEPed polymers.

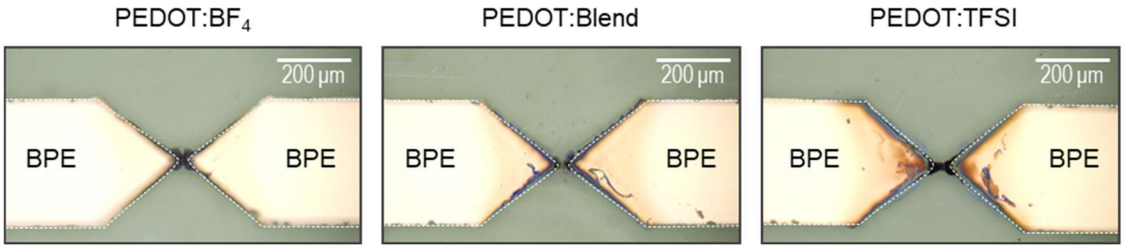

Fig. S2 Optical images of OSIEPed films for PEDOT:BF_4, PEDOT:Blend, and PEDOT:TFSI.

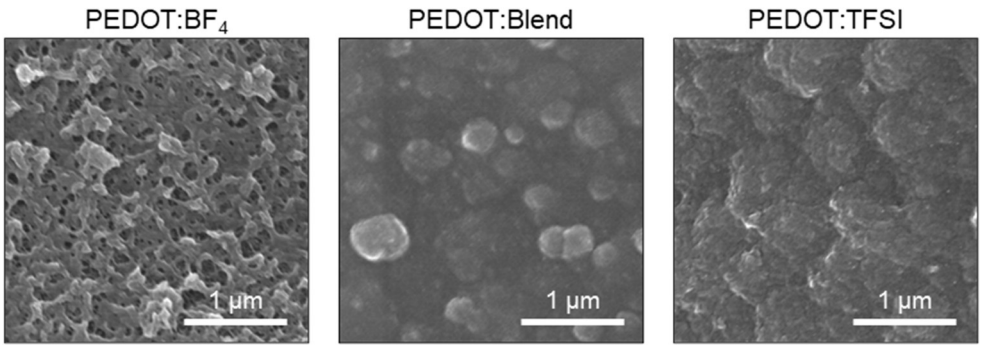

Fig. S3 High-resolution SEM images of OSIEPed films for PEDOT:BF_4, PEDOT:Blend, and PEDOT:TFSI.

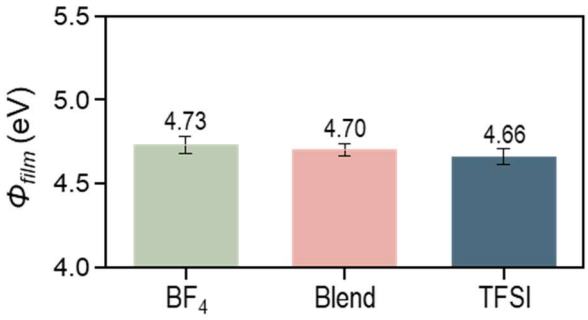

Fig. S4 Surface potential variations of OSIEPed films analyzed by KPFM.

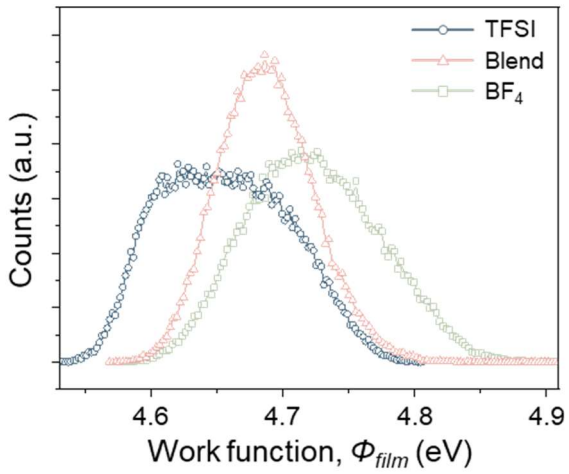

Fig. S5 Histogram of the surface potential variations obtained by KPFM analysis.

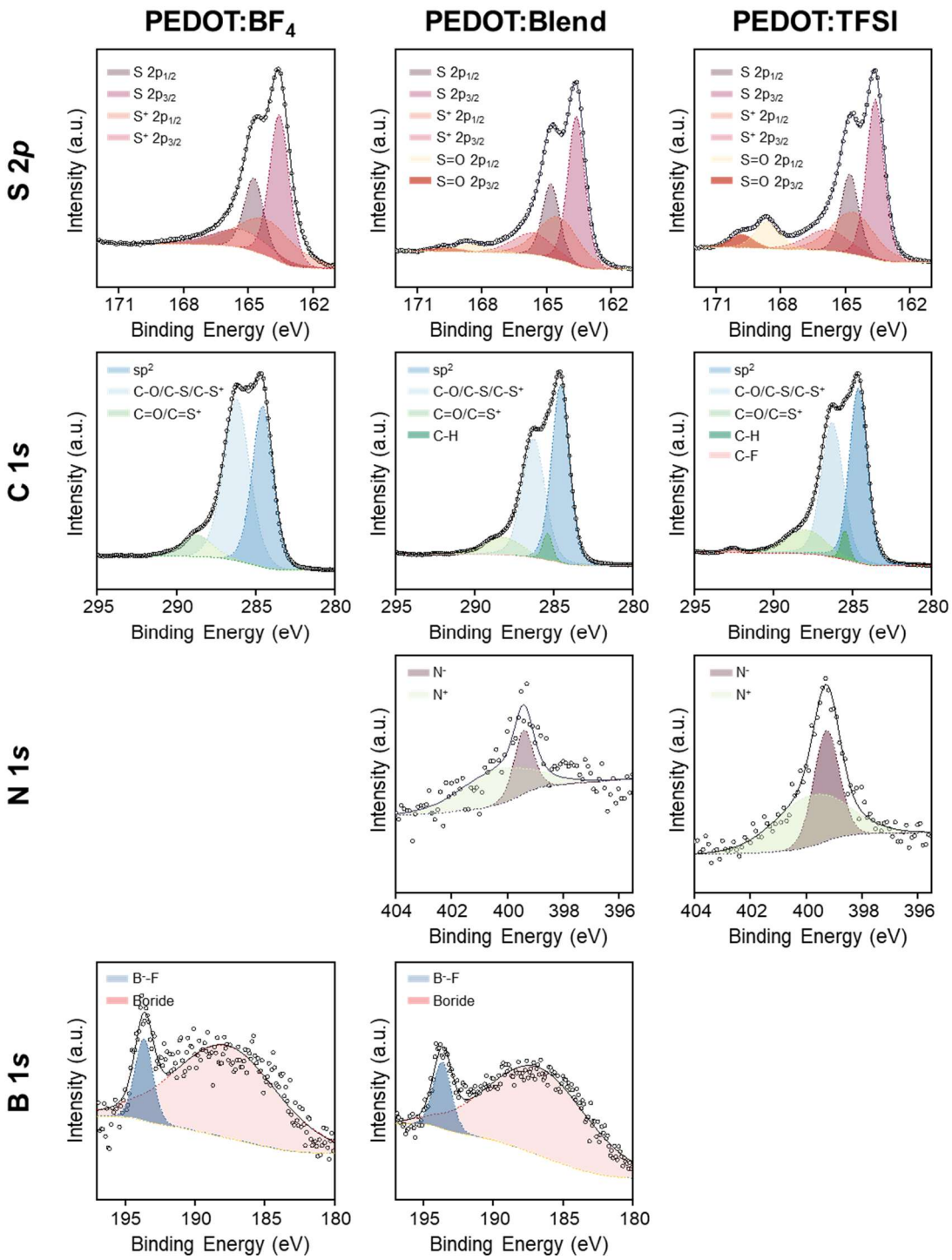

Figure S6. S 2*p*, C 1*s*, N 1*s* and B 1*s* XPS spectra of PEDOT: BF_4, PEDOT:Blend, and PEDOT:TFSI thin films.

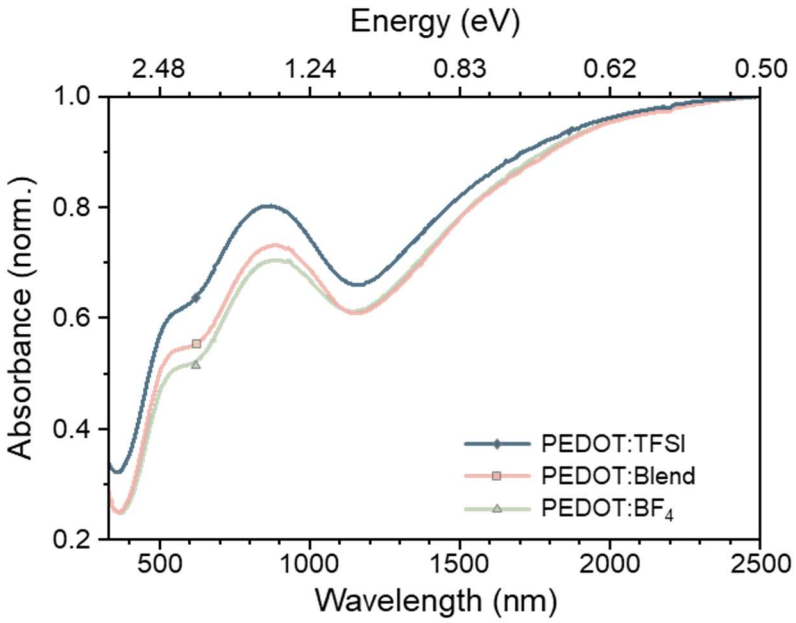

Fig. S7 Normalized UV-Vis-NIR absorbance spectra of the three OSIEPed films.

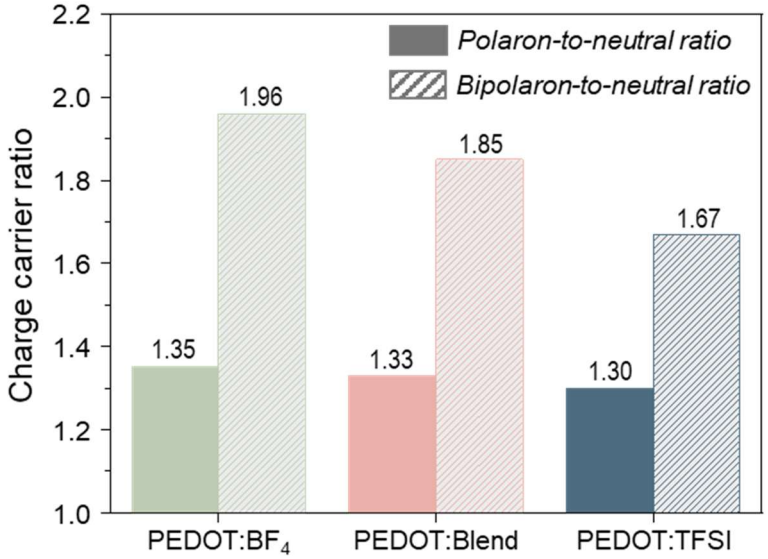

Fig. S8 Charge carrier ratios (*P*/*N* and *B*/*N*) of the three OSIEPed films.

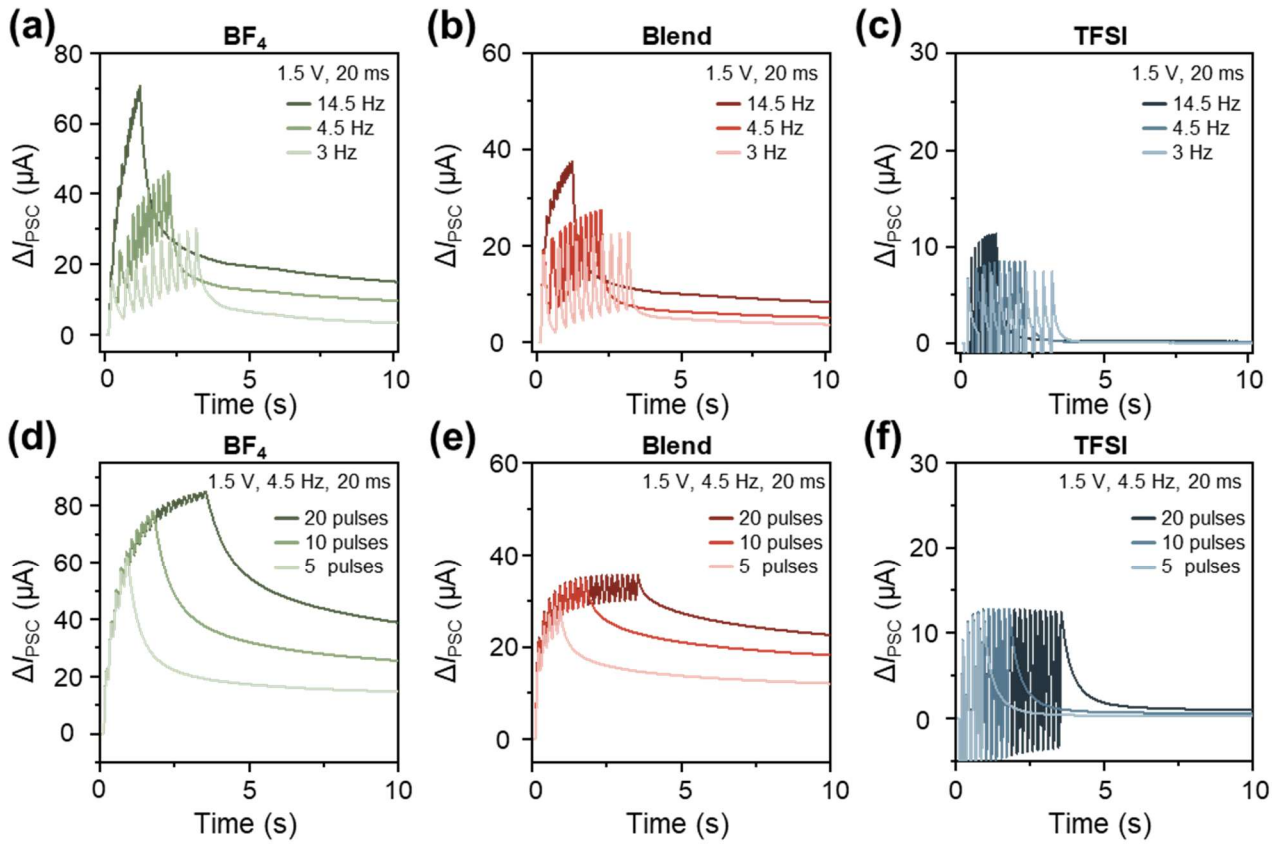

Fig. S9 Spike rate-dependent characteristics of the (a) PEDOT:BF_4, (b) PEDOT:Blend, and (c) PEDOT:TFSI synaptic transistors. Spike number characteristics of the (a) PEDOT:BF_4, (b) PEDOT:Blend, and (c) PEDOT:TFSI synaptic transistors.

Table S1. Intensities (I) and wavelengths (λ) at the maximum peak of each charge carrier type for the three PEDOT:anion films, as analyzed from the UV-Vis-NIR absorbance spectra.

	PEDOT:BF_4	PEDOT:Blend	PEDOT:TFSI
$I_{neutral}$	0.51	0.54	0.60
$I_{polaron}$	0.69	0.72	0.78
$I_{bipolaron}$	1	1	1
$\lambda_{neutral}$	578	567	543
$\lambda_{polaron}$	868	897	927
$\lambda_{bipolaron}$	2496	2500	2493

Table S2. Crystallographic information.

Crystallographic parameters		Out-of-plane			In-plane		
		PEDOT :BF_4	**PEDOT: Blend**	**PEDOT: TFSI**	**PEDOT :BF_4**	**PEDOT: Blend**	**PEDOT: TFSI**
Lamella packing (100)	q ($Å^{-1}$)	0.48	0.45	0.45	0.44	0.43	0.42
	d-spacing (Å)	13.1	14.1	13.9	14.3	14.8	15.1
	FWHM ($Å^{-1}$)	0.10	0.12	0.06	0.12	0.11	0.10
	Correlation length (Å)	54.9	47.3	95.1	47.9	53.3	55.1
π-π stack (010)	q ($Å^{-1}$)	1.79	1.77	1.77	1.81	1.80	1.81
	d-spacing (Å)	3.51	3.56	3.54	3.47	3.50	3.47
	FWHM ($Å^{-1}$)	0.17	0.16	0.19	0.18	0.19	0.15
	Correlation length (Å)	54.9	57.7	47.4	52.9	49.5	60.6