Supporting Information

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Ink-Jet Printable, Self-Assembled, and Chemically Crosslinked Ion-Gel as Electrolyte for Thin Film, Printable Transistors

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Contents:

1. Experimental Section

Preparation of PVA/PEMA ion-gel ink and film: Poly(vinyl alcohol) (PVA, Mw:100,000, Sigma Aldrich) and poly(ethylene-*alt*-maleic-anhydride) (PEMA, Mw: 100,000 - 500,000 , Sigma Aldrich) were separately dissolved in dimethyl sulfoxide (DMSO) and stirred at 60 ºC. The weight ratio of PVA and PEMA was 70:30. After cooling down to room temperature (RT), PVA and PEMA solutions were mixed and stirred at RT for 2 h. The solution was filtered by a 13 mm syringe filter (Acrodisc, 0.45 μm Nylon membrane). After filtration, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate ([EMIM][OTf], Sigma Aldrich) was added into the solution.

Characterization of PVA, PEMA, and PVA/PEMA ion-gel: The dried films of PVA/PEMA gel and ion-gel were cut in disks with 12 mm of diameters (Area: 1.13 cm^2) and assembled in two stainless steel electrodes for impedance measurements. A Biologic SP 150 device with low current option was used to perform impedance spectroscopy. The sweeping frequency range was from 300 kHz to 1 Hz, and the voltage amplitude was fixed to 10 mV. Fourier-transform infrared (FTIR) spectroscopy (Perkin Elmer) was performed, scanning 12 times from 2000 cm^{-1} to 500 cm^{-1}. For the measurement, four different films of PVA, PEMA and PVA/PEMA gel and ion-gel were prepared by drying on petri dish at 50 °C for 2 days. Scanning electron microscopy (SEM) was performed on a ZEISS Leo 1530. Images were taken at an acceleration voltage of 5 kV and a magnification of 10000. The samples were sputtered with a thin gold layer of approximate 10 nm thickness using a Cressington Sputter Coater 108 auto.

Fabrication and characterization of electrolyte-gated transistors (EGTs): In_2O_3 channels were prepared by ink-jet printing and subsequent annealing using indium oxide precursor inks consisting of 0.05 M $In(NO_3)_3$ dissolved in deionized water (D.I. water) and glycerol. The In_2O_3 precursor ink was filtered through a hydrophilic syringe filter (0.45 μm, polyvinylidene fluoride (PVDF)), and printed by a Dimatix 2831 ink-jet printer (Fujifilm).

Gate, source and drain electrode were patterned on indium tin oxide (ITO) substrate by e-beam lithography. Channel width and length are 600 μm and 20 μm, respectively. After printing, the printed structure was annealed at 400 °C for 2 h, afterwards, the PVA/PEMA ion-gel ink was ink-jet printed on the In_2O_3 channel. The nozzle temperature was 25 °C, and the substrate temperature was set to 40 °C. After drying, PEDOT:PSS as top-gate electrode was printed on the ion-gel and dried at 60 °C for 30 min. The fabricated EGTs were characterized by an Agilent 4156 C semiconductor analyzer and a Yokogawa DL6104 digital oscilloscope. The potential scan rate for measurement was set to 0.2 V s^{-1}.

2. Supplementary figure

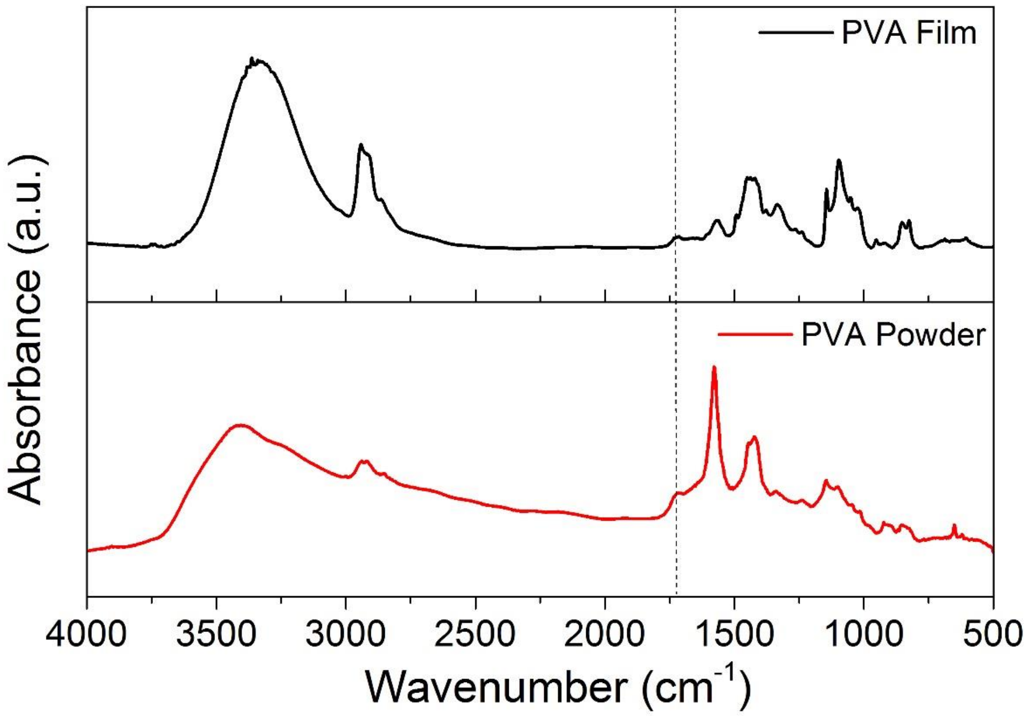

Figure S1. FT-IR absorbance spectrum of PVA film (black) and PVA pellet (red). PVA powder was pelletized with commercial PVA and KBr by hydraulic pressure.

Figure S1: FT-IR analysis was carried out to determine that C=O band of PVA film at ~1720 results from C=O band of poly(vinyl acetate) (PVa). To make a PVA pellet, commercial PVA powder (Sigma Aldrich) and potassium bromide (KBr, Merck) were pelletized by a hydraulic pressure. In the absorbance spectra of the PVA pellet, the C=O band is clearly observed at ~ 1720 cm^{-1}, indicating that commercial PVA powder contains a small amount of PVa, which is not hydrolyzed in PVA production, and also clarifying that C=O band at ~1720 cm^{-1} in PVA film is not created during the film-making process.

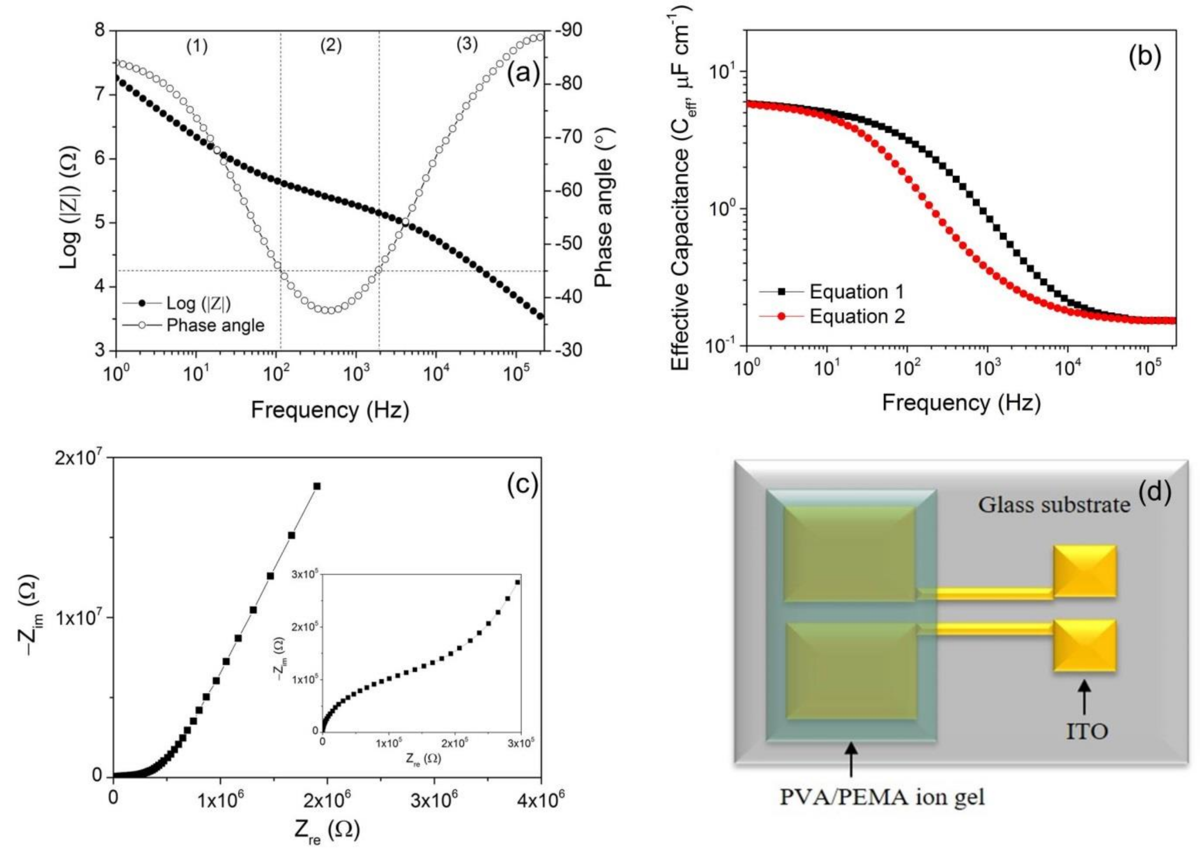

Figure S2. Impedance results of PVA/PEMA ion-gel in in-plain substrate; (a) Bode plot of log(|Z|) versus frequency, (b) C_{eff} versus frequency plot, (c) Nyquist plot, and (d) Schematic image of in-plain ITO electrodes patterned by e-beam laser. PVA/PEMA ion-gel is printed on a patterned electrode (500×300 μm) by ink-jet printer.

Figure S2: In-plane ITO electrodes patterned on the glass substrate by e-beam laser were prepared to identify C_{eff} and frequency-dependent behavior of ink-jet printed ion-gel. Compared to ion-gel film, frequency-dependent plots of log (|Z|), phase angle, and C_{eff} are shifted to low-frequency range. The plots clearly show resistive and capacitive behaviors according to the applied frequency, and even dipole relaxation behavior is observed in high-frequency ranges. Considering the frequency shift, the impedance result of an ink-jet printed ion-gel is corresponding to that of ion-gel film.

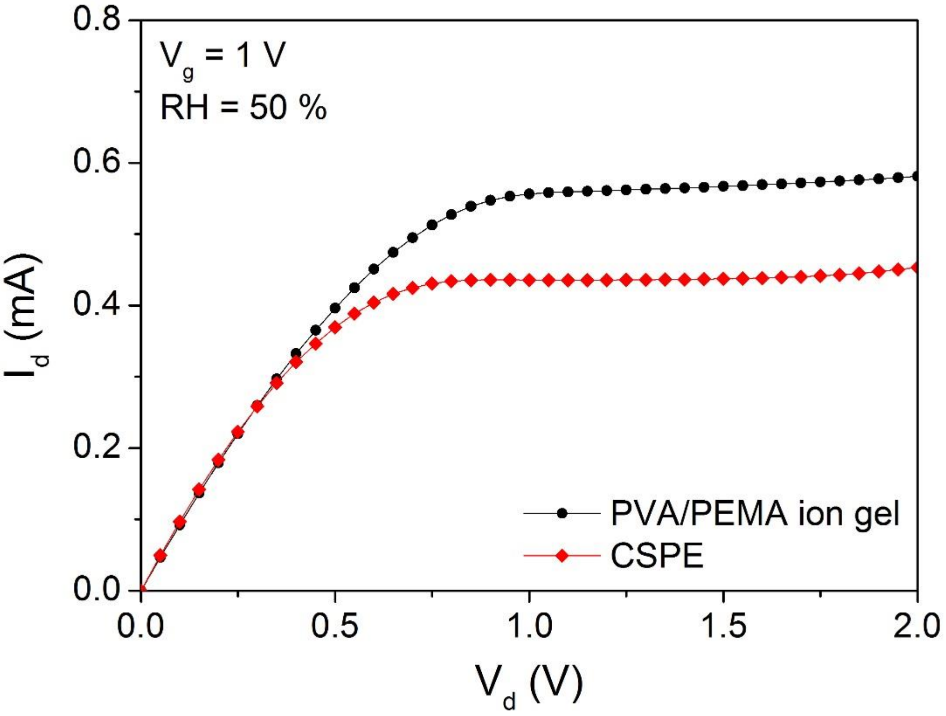

Figure S3. Drain-source voltage (V_d) versus drain-source current (I_d) plots of PVA/PEMA ion-gel and CSPE-gated transistors at 1 V_g and relative humidity (RH) of 50 %.

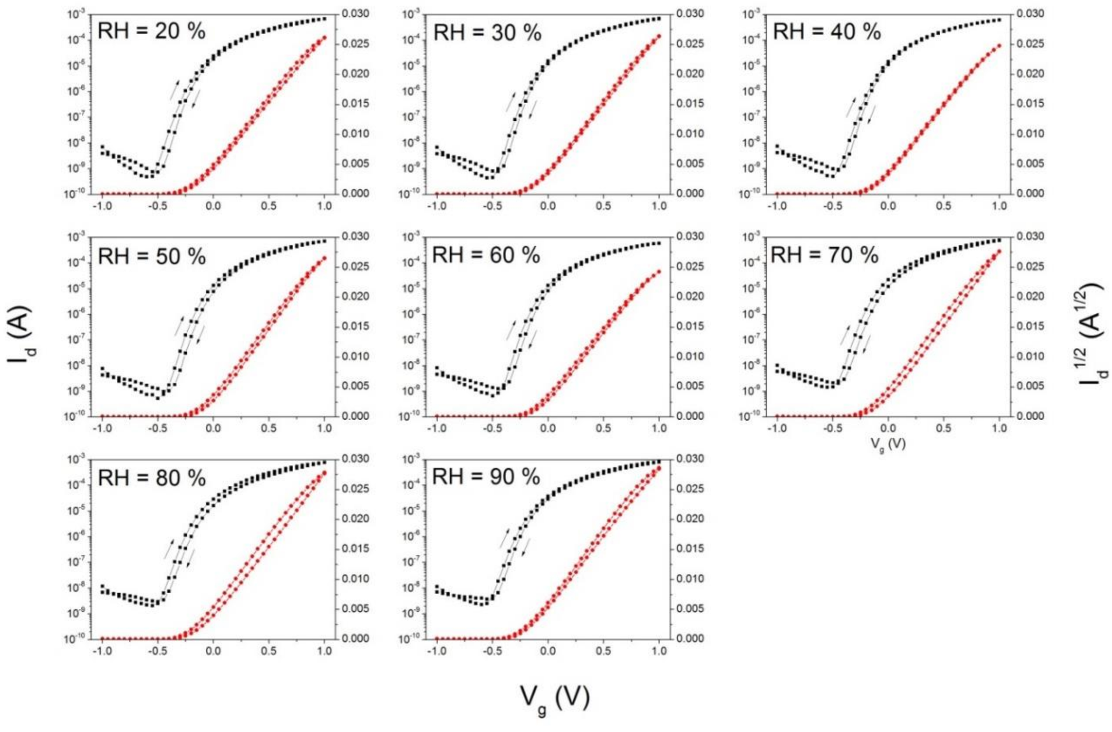

Figure S4. V_g versus I_d and $I_d^{1/2}$ plots of PVA/PEMA ion-gel-gated transistors at 1 V_d and different RH from 20 % to 90 %.

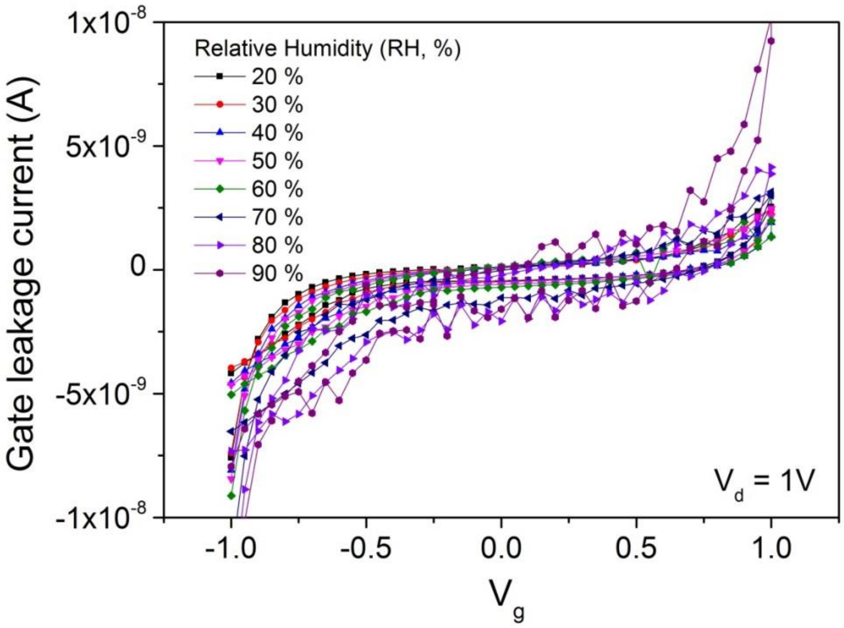

Figure S5. V_g versus gate current (I_g) plots of PVA/PEMA ion-gel-gated transistors at 1 V_d and different RH from 20 % to 90 %.

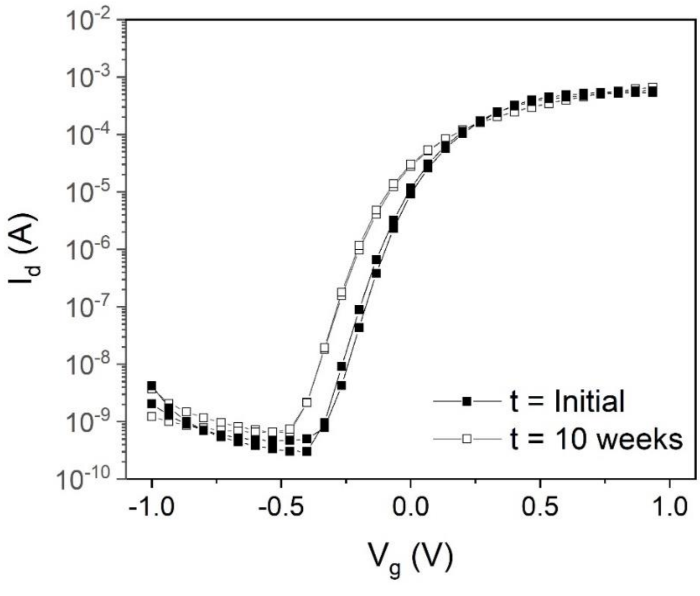

Figure S6. Gate-source voltage (V_g) versus drain-source current (I_d) plot for durability test of ion gel-gated transistors. Drain voltage (V_d) is 1 V. RH is 50 %. The sample is aged for 10 weeks in room condition.

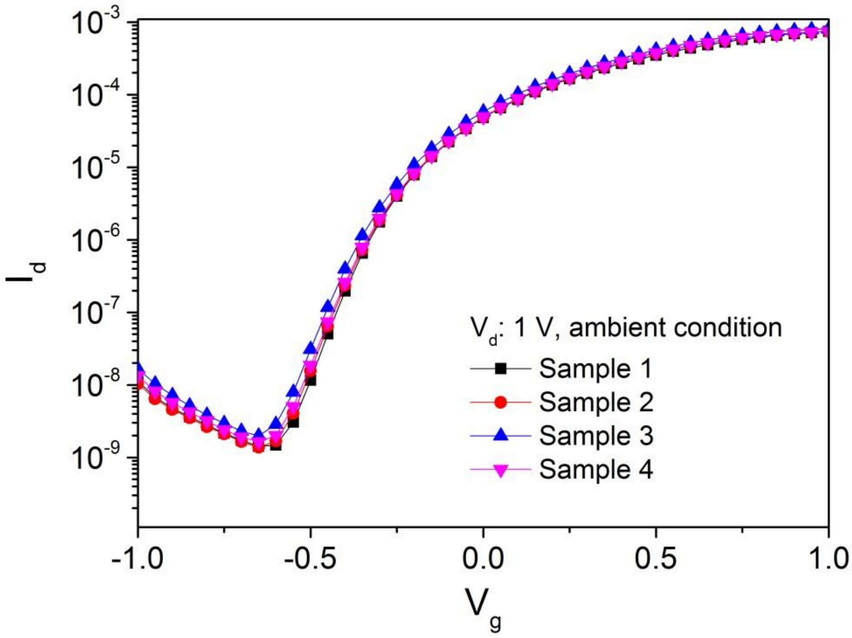

Figure S7. V_g versus I_d plot for reproduced ion gel-gated transistors (V_d is 1 V) under ambient conditions. Channel width and length are 600 μm and 20 μm, respectively. Four samples of EGTs were sequentially measured in the same condition to show experimental consistency.

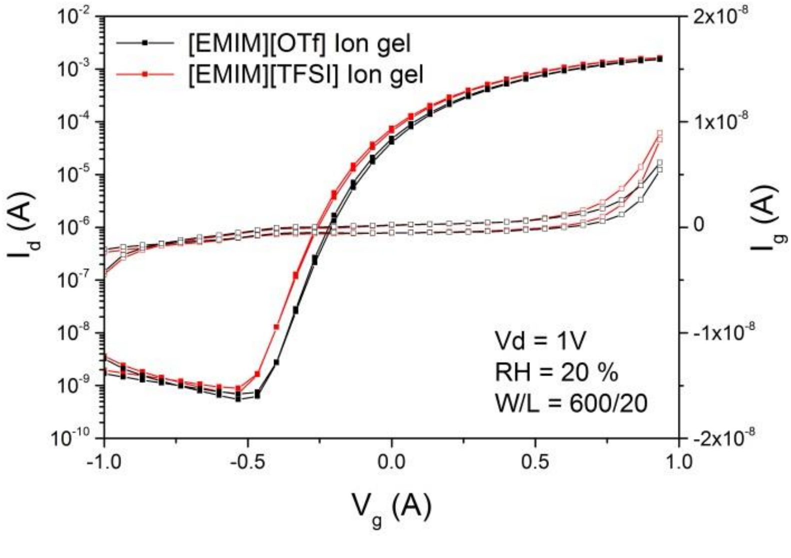

Figure S8. V_g versus I_d and I_g plot of ion gel-gated transistors. Two different ionic liquid of [EMIM][OTf] and [EMIM][TFSI] were used for ion gel. The ink ratios, fabrication, and measurement conditions of ion gels are the same. V_d is 1 V and RH is 20 %.

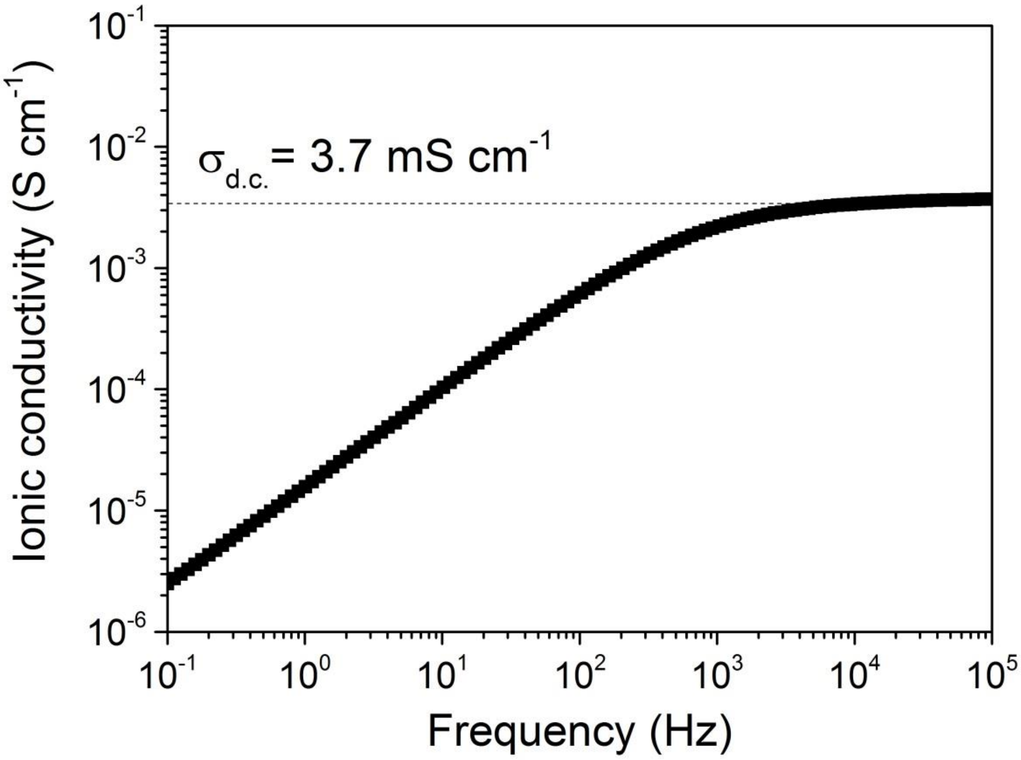

Figure S9. Ionic conductivity versus frequency plot of [EMIM][TFSI]-based ion gel. Ionic conductivity is calculated with the result of impedance spectroscopy. The thickness and diameter of ion gel film are 0.9 mm and 12 mm.

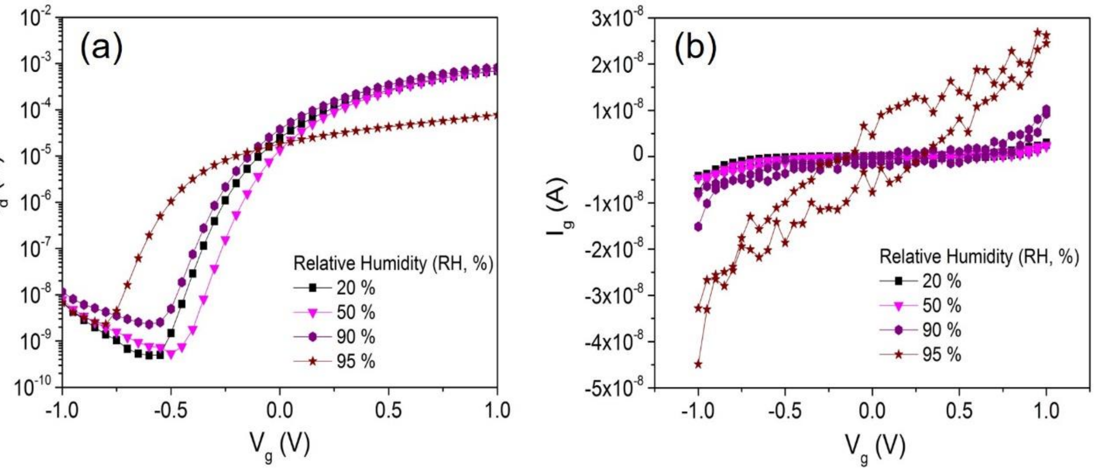

Figure S10. (a) V_g versus I_d plots and (b) V_g versus I_g plots of PVA/PEMA ion-gel-gated transistors at 1 V_d and different RH condition.