<div align="center">**Supporting Information**</div>

Crown ether enabled enhancement of ionic-electronic properties of PEDOT:PSS

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Experimental section

Materials: Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevios PH1000) was purchased from Heraeus 15-Crown-5 (98%), sodium chloride (NaCl), (3-glycidoxypropyl)trimethoxysilane (GOPS), ethylene glycol (EG, ≥99%) and 4-Dodecylbenzenesulfonic acid (DBSA, ≥95%) were purchased from Sigma-Aldrich. The p-Si/SiO$_2$ (300 nm) substrate wafers were purchased from Jiangyin Maideli Advanced Materials Co. Ltd.

OECT fabrication: OECTs were prepared using the Parylene C peel-off procedure as reported previously.[1] Briefly, the p-Si^{++}/SiO$_2$ substrates were cleaned by soap water, DI water, acetone, and iso-propyl alcohol with sonication for 10 min each subsequently, followed by N$_2$ blow drying. The source/drain electrodes were then photolithographically patterned as follows: 1) AZ 5214 photoresist was spin-coated onto the cleaned substrates and exposed to UV light using a SUSS MJB4 mask aligner, and then developed by AZ developer; 2) this was followed by depositing a thin layer of titanium (5 nm) and Au (50 nm) electrode via an E-beam evaporator; 3) lift-off was performed by immersion of the substrates in acetone for 5 min with sonication. A 2 μm thick Parylene C layer, together with an adhesion promoter of 3-(trimethoxysilyl)propyl methacrylate (A-174 Silane) was deposited, to insulate the contacts from electrolyte using SCS Labcoater. An anti-adhesion layer of dilute cleaner (Micro-90, 10 wt.% in deionized water) was spin-coated to

facilitate the peel-off procedure. After that, a second Parylene-C layer (~2.5 μm) was deposited, acting as a sacrificial layer. Substrates were subsequently coated with a 12 μm thick AZ P4620 photoresist, soft-baked at 110 °C for 180 s, exposed using SUSS MJB4 mask aligner, and developed by AZ developer. The patterned channel area and contact pads were etched via reactive ion etching (Oxford Plasmalab80) at 50 sccm O_2, 10 sccm CHF_3, 160 W operating condition. Modified PEDOT:PSS solutions were prepared by adding 25 μL 15-crown-5 and 5 μL GOPS into 1mL PEDOT:PSS followed by vigorous shaking for 15 minutes at room temperature. Pristine PEDOT:PSS solutions were prepared in the same way with the exception of 15-crown-5 addition. EG-PEDOT:PSS solution was prepared by adding 50 μL ethylene glycol, 0.25 μL DBSA and 5 μL GOPS into 1mL PEDOT:PSS followed by vigorous shaking for 15 minutes. The prepared solutions were spin-coated onto the patterned substrates to form the channels followed by annealing at 90 °C for 2 min. After that, the sacrificial Parylene-C layer was peeled-off and the films were further annealed at 140°C for 10 minutes. The cooled films were rinsed with DI water before device and materials characterization.

Electrical characterization: The I-V characteristic of the films, and all the OECT device characteristics including output and transfer curves and pulse measurements were measured under ambient conditions using Keysight precision source measure unit (B2912A).

Electrocardiography (ECG) recording: Two commercial Ag/AgCl electrodes (Red Dot, 3M) were used with one Cr-PEDOT:PSS OECT for ECG recording. One Ag/AgCl electrode was connected to the source of the Cr-PEDOT:PSS OECT and attached the right hand, another Ag/AgCl electrode was connected to the gate of the Cr-PEDOT:PSS OECT and placed at the chest near the heart of the volunteer. The drain current of the Cr-PEDOT:PSS OECT was measured and processed. An effective gate bias was enabled due to the potential difference between the hand and the heart of the volunteer. The Keysight precision source/measure unit (B2900A Series) was used to supply the drain voltage (-0.5V). And a band-pass filter at 25Hz wad used to filter the resultant signals to remove the power supply noise.

Materials Characterization: The electrical conductivity of the solid films were calculated by measuring sheet resistance free of contact resistance using the Ossila Four-Point Probe system. The thickness of the polymer films was characterized with Alpha-Step profilometer (KLA-Tencor). GIWAXS measurements were carried out on films spin-coated on p-Si substrates using Xenocs Nanoinxider with Cu-Kα microsource (40 mm), 30W, at an incidence angle of 0.2 degrees.

X-ray photoelectron spectroscopy (XPS) analysis was performed using an AXIS Supra spectrometer (Kratos Analytical Inc., UK) equipped with a hemispherical analyser and a monochromatic Al K-alpha source (1487 eV) operated at 15 mA and 15 kV. The XPS spectra were acquired from an area of 700 x 300 $\mu m2$ with a take-off angle of 90°. Pass energy of 160 eV and 20 eV were used for survey and high-resolution scans, respectively. The sample, prepared on ITO-coated glass substrate, was electrically grounded to the sample holder to prevent charge build-up on the sample surface. Absorption spectra of the polymer films were recorded on UV-VIS spectrophotometer (UV-3600, Shimadzu). Thin films were spin-coated on ITO similar to those used for XPS measurements. Electrochemical Impedance Spectroscopy (EIS) measurements were carried out using the Metrohm Autolab potentiostat with a three-terminal system consisting of a working electrode (PEDOT:PSS films were deposited on pre-patterned Ti/Au electrodes of varying areas using photolithography as described above for OECTs fabrication), a Pt counter electrode, and an Ag/AgCl reference electrode, over a frequency range from 10^5 Hz and 1 Hz with a 10 mV single sinusoidal signal at $E_{dc} = 0$ V.
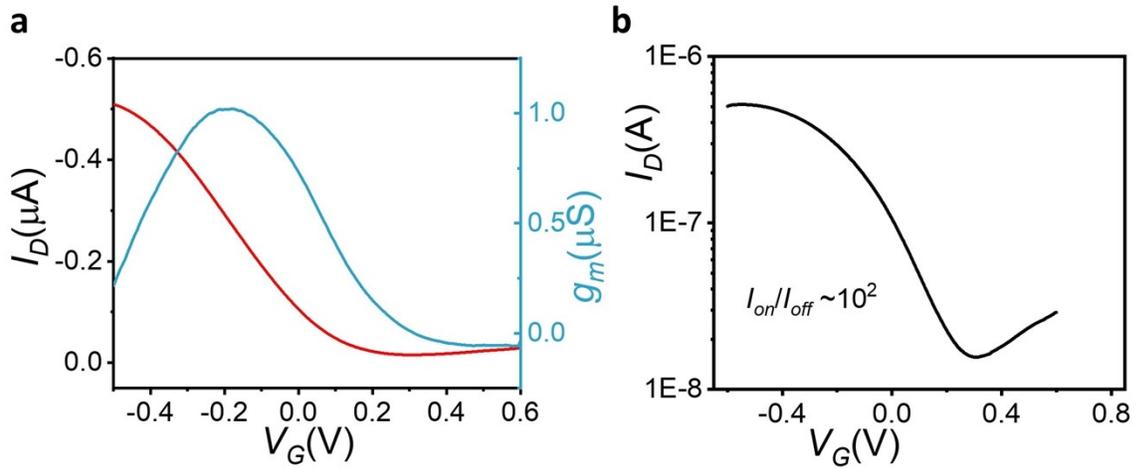
Figure S1. (a) Transfer curve (left axis) and transconductance (right axis) for pristine PEDOT:PSS OECT (W = 100 µm, L = 10 µm); (b) Transfer curve with the drain current plotted in log scale for the same OECT.

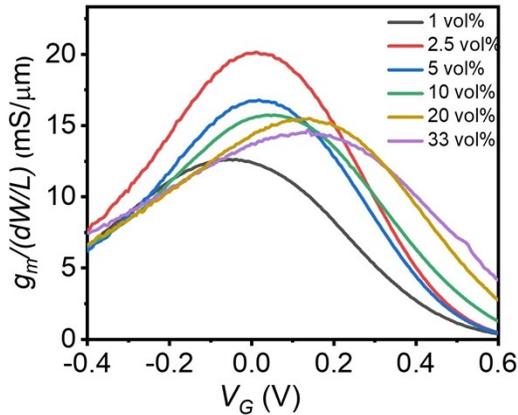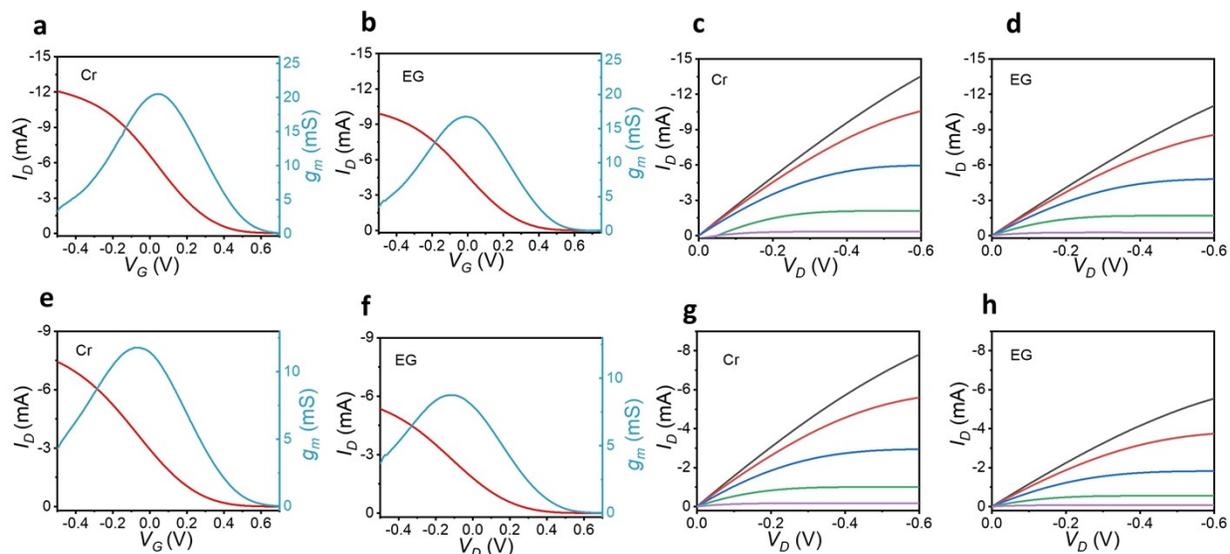**Figure S2.** Variation of OECT transconductance with varying 15-crown-5 loading in PEDOT:PSS channel. (W=100 µm, L=10 µm)

Figure S3. (a) & (b) Transfer characteristics of OECTs with W=100 µm, L = 10 µm, based on Cr-PEDOT:PSS and EG-PEDOT:PSS channels, respectively; (c) & (d) Output characteristics of OECTs with W=100 µm, L = 10 µm, based on Cr-PEDOT:PSS and EG-PEDOT:PSS channels, respectively; (e) & (f) Transfer characteristics of OECTs with W=10 µm, L=10 µm, based on Cr-PEDOT:PSS and EG-PEDOT:PSS channels, respectively; (g) & (h) Output characteristics of OECTs with W=10 µm, L=10 µm, based on Cr-PEDOT:PSS and EG-PEDOT:PSS channels, respectively.

Table S1. Comparison of OECT performance of PEDOT:PSS based OECTs

Additive	Channel dimensions W/L(µm/ µm)	Channel thickness d (nm)	Normalised transconductance $g_m/(dW/L)$ (mS/ µm)	I_{ON}/I_{OFF}	Threshold voltage V_T(V)	Ref
Glycerol	80/5	70	0.8	10^3	> 0.5	[2]
Sorbitol	500/5	2000	0.2	10^5	> 0.6	[3]
Triton-X-100	1000/250	2000	4.9	10^3	0.36	[4]
H₂SO₄	80/20	200	23.8	10^4	> 0.6	[5]
Ethylene glycol	80/20	190	5.3	10^4	> 0.4	[5]
EMIM-OTF	100/10	108	19.3	10^5	0.48	[6]
EMIM-TCM	100/10	105	21.4	10^5	0.71	[6]
Pristine	100/10	100	0.001	10^2	0.18	This work
Ethylene glycol	100/10	100	16.7	10^5	0.33	This work
15-crown-5	100/10	100	20.5	10^5	0.36	This work

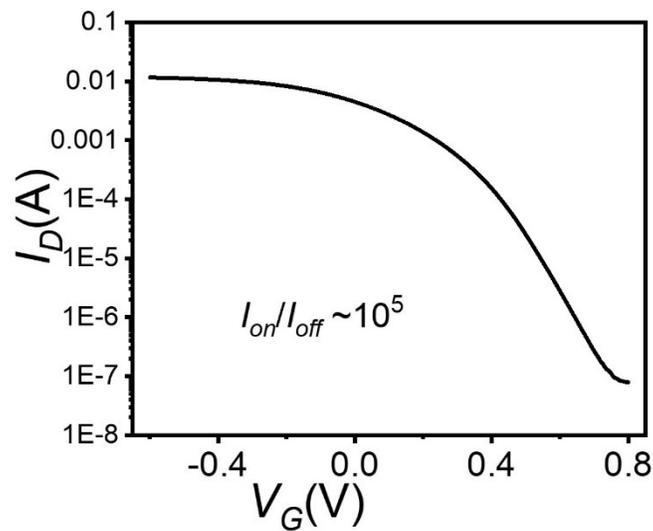**Figure S4.** Transfer curve of Cr-PEDOT:PSS OECT with W=100 μm & L = 10 μm, with drain current plotted in log scale.
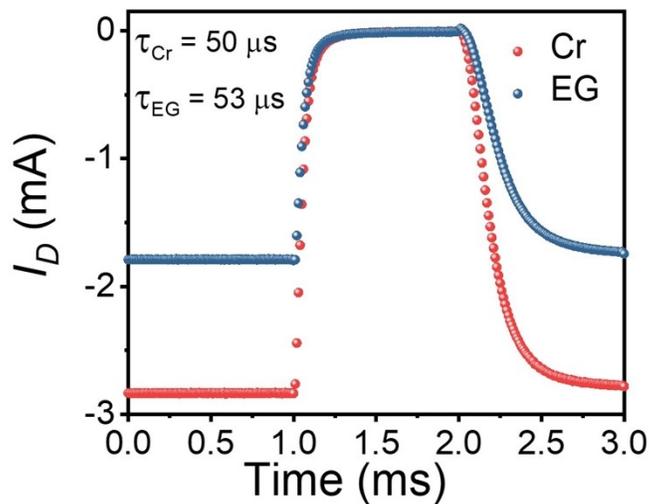

Figure S5. Transient response of drain currents for Cr-PEDOT:PSS (red) and EG-PDOT:PSS (blue) based OECTs at V_G = 0.6 V. Cr-PEDOT:PSS shows a fast response time (τ) of 50 μs despite showing much higher currents.
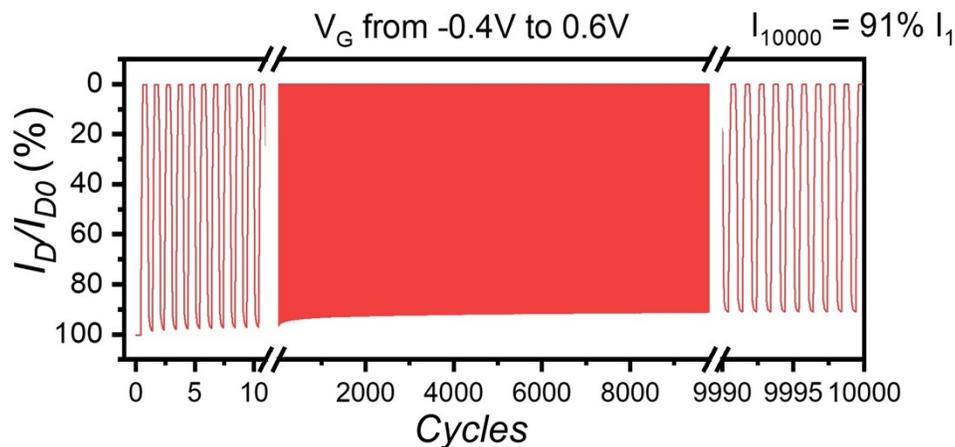
Figure S6. Operational stability of Cr-PEDOT:PSS OECTs for 10000 cycles of V_G pulsing between -0.4V and 0.6V, at V_D = -0.5V
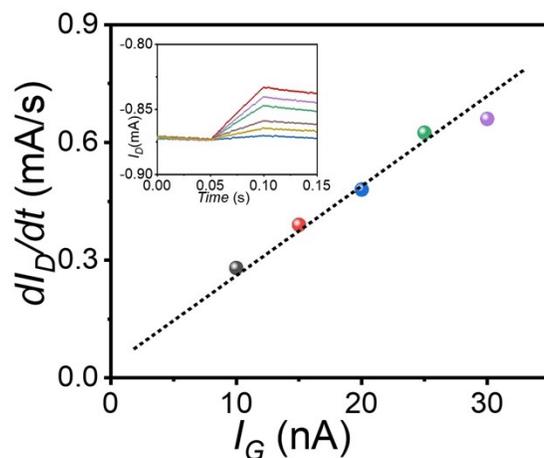

Figure S7. Time derivative of drain current as a function of gate current for EG-PEDOT:PSS at V_D of -0.1 V, in accordance to the equation $dI_D/dt = -I_G/\tau_h$. Inset shows the variation of drain current with time for different applied gate currents, yielding a mobility of 0.25 ± 0.023 cm^2/Vs
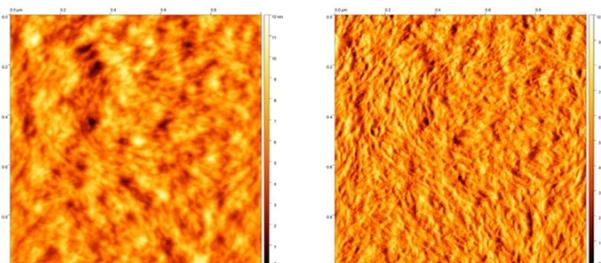

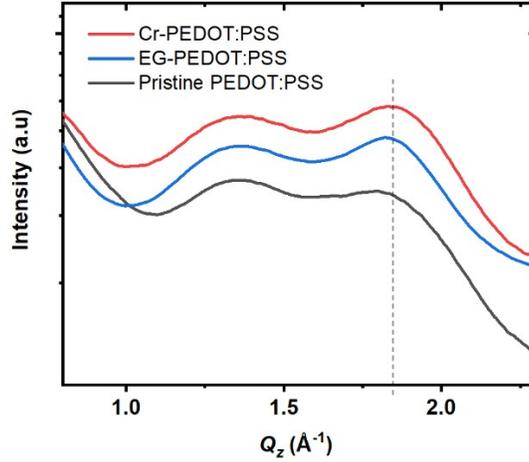**Figure S8.** AFM topography (left) and phase (right) images of EG-PEDOT:PSS film.

Figure S9. GIWAXS 1D line-cuts of pristine PEDOT:PSS, EG_PEDOT:PSS and Cr-PEDOT:PSS films along the q_z direction.
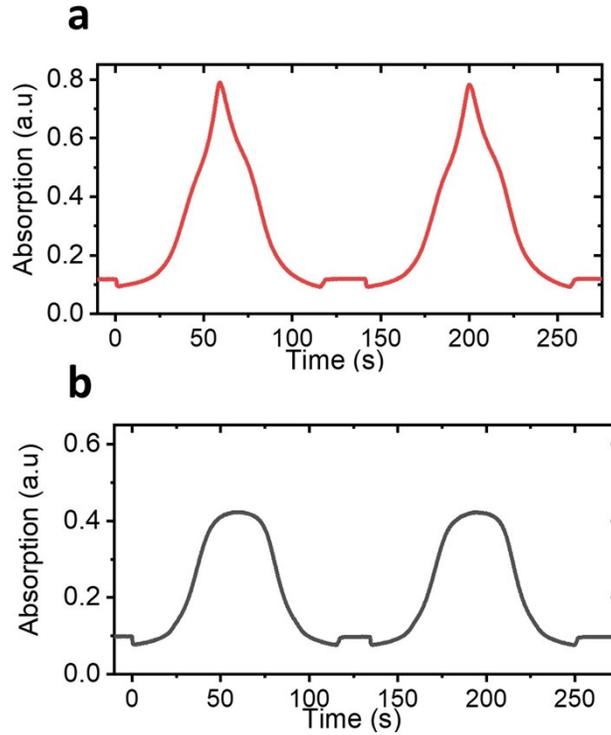

Figure S10. Time-resolved absorption recorded at 650 nm for two cycles of progressively increasing the applied bias from -0.2 to 1V and then back to -0.2V for (a) Cr-PEDOT:PSS; and (b) Pristine PEDOT:PSS films. Note that the data ~120-140s corresponds to the gap between two voltage cycles and essentially shows the absorption of the film without any applied bias.

References

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