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Ionic liquid doping enables high transconductance, fast response time and high ion sensitivity in organic electrochemical transistors

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Abstract

Organic electrochemical transistors (OECTs) are highly attractive for applications ranging from circuit elements, neuromorphic devices to transducers for biological sensing and the archetypal channel material is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), PEDOT:PSS. The operation of OECTs involves the doping and de-doping of a conjugated polymer due to ion intercalation under the application of a gate voltage. However, the challenge is the trade-off in morphology for mixed conduction since good electronic charge transport requires a high degree of ordering among PEDOT chains, while efficient ion uptake and volumetric doping necessitates open and loose packing of the polymer chains. Here we demonstrate ionic liquid doped PEDOT:PSS that overcomes this limitation. Ionic liquid doped OECTs show high transconductance, fast transient response and high device stability over 3600 switching cycles. The OECTs are further capable of having good ion-sensitivity and robust towards physical

deformation. These findings pave the way for higher performance bioelectronics and flexible/wearable electronics.

The use of organic electrochemical transistors (OECTs) for various applications ranging from neuromorphic devices^[1] to transducers for biological sensing, including detection of ions,^[2,3] metabolites (such as glucose^[4,5]), DNA,^[6] antibody-antigen interaction,^[7] and cancer cells^[8] has received significant attention in recent years. An OECT consists of a conjugated polymer channel in direct contact with an electrolyte, where the operation involves doping and de-doping of the conjugated polymer by reversible exchange of ions present in an electrolyte under the application of a very low gate voltage ($V_G < 1\text{V}$). The measured drain current (I_D) of the polymer channel between the source and drain contacts is therefore modulated through accumulation or depletion of charges throughout the bulk of the polymer. The corresponding transconductance ($g_m = \partial I_D / \partial V_G$) is typically large (up to 2.0 mS for micrometer-scale devices^[9]), making OECTs an efficient ion-to-electron transducers, capable of amplifying small chemical signals and with high signal-to-noise ratios. One important advantage of OECTs is that they can be fabricated from biocompatible organic materials, enabling an amiable interface with cells and tissues in aqueous environments (water-based electrolytes).^[10] Also, their simple structure allows the potential for large-area and low-cost electronics through their facile fabrication processes such as printing and easy integration with microfluidic lab-on-a-chip applications.^[11,12]

The OECT transconductance, g_m , is defined as follows:^[13]

$$g_m = \frac{Wd}{L} \mu C^* (V_{th} - V_G) \quad (1)$$

where d , W , and L are the thickness, width, and length of the channel respectively, μ is the carrier mobility, C^* is the volumetric capacitance, and V_{th} is the threshold voltage of the channel. In particular, the μC^* figure of merit dictates the carrier and ionic transport and therefore affects the g_m parameter.^[14] In general, a good OECT channel material needs to

have good electronic transport properties (high μ) and allows effective ion penetration from the electrolyte into active channel (high C^*). The ability to have mixed ionic and electronic transport properties in organic materials have also been widely utilized in many other applications such as electrode materials of batteries/supercapacitors,^[15–17] electronic ion pumps,^[18] and electrochromic windows.^[19] However, it is a limitation to identify materials with both high electronic and ionic conduction since there is a fundamental trade-off between the two properties. The electronic properties are strongly associated with a high degree of ordering among the conjugated polymer chains, which allows efficient delocalization of π -electrons across the polymer chains. In contrast, efficient ion transport requires open and loose packing of the polymer chains.^[20] The current state-of-the-art active conjugated polymer for OECTs is poly(3,4-ethylenedioxythiophene) (PEDOT) which is commonly charge compensated by an immobile polymer anion, polystyrenesulphonate (PSS), **Figure 1(a).**^[11,21] The pristine PEDOT:PSS thin films typically suffer from low electrical performance (conductivity: ~ 1 S/cm; hole mobility: 10^{-3} cm² V⁻¹s⁻¹),^[22] due to excessive insulating PSS content and lack of dense packing of PEDOT chains. One commonly used strategy is the addition of co-solvent dispersion additive, ethylene glycol (EG), which leads to an increase in PEDOT aggregation or structural reorganization of the PEDOT domains into more continuous network and thus enhances the charge carrier mobility (μ).^[23] However, in these instances, the C^* tends to decrease as densification of the PEDOT chains does not favour ion conduction. Efforts to increase ionic conductivity, by combining polyelectrolytes with conjugated polymer have also been performed.^[24] But the resulting phase separation typically deteriorates the electronic conduction. The overall μC^* figure of merit in many OECT channel materials is therefore moderate, with opposing relationships between μ and C^* . The simultaneous improvement of the ionic and electronic transport in conjugated polymer is thus unrealized and important for maximizing the performance of OECTs.

In addition, the Young's modulus of PEDOT:PSS is considerably higher than most live tissues and recent reports reveal that PEDOT:PSS are vulnerable to strain (~ 5 to 6% fracture strain),^[25] which can be a limitation for a variety of applications in bioelectronics and wearable devices. Incorporation of plasticizers,^[26] copolymers such as polyurethane^[27] or surfactants such as Triton^[28] have been done to improve the flexibility and stretchability of PEDOT:PSS films but there have not been many reports on their implementation in flexible or stretchable OECTs, possibly due to the challenges in ensuring good electronic and ionic transport while enhancing the mechanical properties at the same time.

In this communication, we demonstrate for the first time, ionic liquid doped PEDOT:PSS as active channel in OECT, with good electronic and ionic transport. The μC^* figure of merit is determined to be $335 \text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$, which is nearly four-order of magnitude higher than the control PEDOT:PSS device ($\sim 0.03 \text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$) and four-fold higher than that of reported devices utilizing state-of-the-art EG-modified PEDOT:PSS^[29] ($\sim 75 \text{ Fcm}^{-1}\text{V}^{-1}$). Specifically, the ionic liquid induces simultaneous higher hole mobility ($\mu = 3.8 \text{ cm}^2/\text{Vs}$) and volumetric doping ($C^* = 87 \text{ Fcm}^{-3}$) in PEDOT:PSS films. The inclusion of ionic liquids creates better electronic conductivity through doping and allows an efficient pathway for hole transport through the formation of a network of fibrillar structure in PEDOT:PSS, while enhancing the ionic character at the same time. The OECTs show record high transconductance, fast transient response and high stability while switching over 3600 cycles. In addition, the non-volatile ionic liquid can serve as a plasticizer in PEDOT:PSS to increase the flexibility and deformability of the OECTs. We also demonstrated a Na^+ ion sensor where the ion sensitivity reached a maximum of 146 mVdec^{-1} as well as capable of monitoring the ions with detection limit as low as $1 \text{ }\mu\text{M}$. These results highlight the potential of ionic liquid doped conjugated polymers for higher performance bioelectronics and flexible/wearable electronics.

Ionic liquids are molten salts with good chemical stability, wide electrochemical window, negligible vapor pressure, and high ionic conductivity.^[30] In the chosen ionic liquid, namely, 1-ethyl-3-methylimidazolium tricyanomethanide ([EMIM][TCM]; see Figure 1(a) for the chemical structure), the cation (EMIM) generally imparts the ionic liquids with electrochemical stability while the anion (TCM) has delocalized charges for increased conductivity. The introduction of [EMIM][TCM] in PEDOT:PSS will result in counter-ion exchange, where the hydrophilic EMIM:PSS and hydrophobic PEDOT:TCM ion pairs form spontaneously. We first investigate the electrical conductivity of the composite films. Figure 1(b) displays the conductivity of PEDOT:PSS films with different added amount of [EMIM][TCM]. In general, the PEDOT:PSS with [EMIM][TCM] composites exhibit substantially higher conductivities, which correlates well with previous studies where ionic liquids are showed to be good conductivity enhancers in conducting polymers.^[22,31,32] For instance, at 1.5 wt.% [EMIM][TCM], the measured conductivity is around 1200 S cm^{-1} which is almost three orders of magnitude higher than that of the pristine PEDOT:PSS film (appropriate 1 S cm^{-1}).

To investigate the presence of [EMIM][TCM] ionic liquid in PEDOT:PSS, the films were characterized by Fourier transform infrared (FT-IR) spectroscopy. Figure 1(c) shows the FT-IR spectra of pristine PEDOT:PSS, PEDOT:PSS containing 1.5wt% [EMIM][TCM] and pure [EMIM][TCM]. Specifically, for the PEDOT:PSS/[EMIM][TCM] film, the appearance of new peaks at around 2160 cm^{-1} and 3154 cm^{-1} which correspond to $\text{C}\equiv\text{N}$ in TCM anion and $=\text{C-H}$ in EMIM cation respectively,^[33] confirmed that the ionic liquid remains in the PEDOT:PSS film. The counterion exchange between PEDOT:PSS and [EMIM][TCM] is reflected in the absorption coefficient spectrum (Figure 1(d)), where one broad band at around 900 nm was observed, attributed to the polaron-induced transitions/higher PEDOT doping level with the addition of [EMIM][TCM].^[34] The film's colour also changed from

light blue for pristine PEDOT:PSS to light green for films containing [EMIM][TCM]. The intensity of this new absorption feature increased incrementally as a function of [EMIM][TCM] (Figure S1, Supporting Information), in agreement with increasing doping levels. The enhanced PEDOT doping level with increasing concentration of [EMIM][TCM] also correlates well with the increased electrical conductivity of the composite films. Another point to note is the appearance of a peak in the UV range (~ 340 nm) for the PEDOT:PSS/[EMIM][TCM] film which likely originates from the aromatic rings of EMIM cations.^[35]

Figure 1. (a) Molecular structures of PEDOT:PSS and [EMIM][TCM]. (b) Conductivity of PEDOT:PSS films with different concentration of [EMIM][TCM]. (c) FT-IR spectra and (d) UV-vis-NIR absorption spectra of pristine PEDOT:PSS, PEDOT:PSS with 1.5 wt.% [EMIM][TCM] and pure [EMIM][TCM].

OECTs have been produced using PEDOT:PSS/[EMIM][TCM] as the active channel material. A water-based electrolyte (0.1 M NaCl solution) is used and the gate electrode was

Ag/AgCl. **Figure 2(a)** shows the schematic of the fabricated OECT. The PEDOT:PSS/[EMIM][TCM] based channel has a thickness (d) of 200 nm with 1000 μm width (W) and 100 μm length (L). In a typical PEDOT:PSS based OECT, the device operates in depletion mode; the OECT is ON in the absence of a gate bias. Upon application of a positive gate bias, V_G , cations from the electrolyte penetrate into the PEDOT:PSS channel. Each cation compensates one PSS^- , while the oxidation of PEDOT^+ is reduced to neutral PEDOT,^[36] thus reducing the hole density and lowering the drain current. As depicted in Figure 2(b)-(c), for the PEDOT:PSS/[EMIM][TCM] based OECT, the decrease in current upon the application of positive gate biasing is consistent with the depletion mode operation. Negligible hysteresis of the transfer and output characteristics are observed, implying ionic movement into/from the channel and doping/dedoping process in PEDOT are efficient (Figure S2). A relatively high gate bias is required to turn off the device ($V_G = 0.8\text{V}$) which is possibly due to the strong ion exchange reaction. Notably, the transistor exhibits a large peak transconductance of 14.2 mS at $V_G = 0.1\text{V}$ and a large on/off current ratio of $\sim 5 \times 10^3$. In addition, Figure 2(d) displays the transconductances of the various PEDOT:PSS/[EMIM][TCM] based OECTs with different channel geometry. A linear correlation is found between transconductance and channel geometry, in agreement with previous reports.^[29] When normalized to the channel geometry, the maximum g_m of our PEDOT:PSS/[EMIM][TCM] based OECT is $\sim 7100\text{ S/m}$ which is a record high, about 2 times higher than that of typical EG-modified PEDOT:PSS based OECTs ($g_m = 2.7\text{ mS}$, $W/L = 2$, $d = 400\text{nm}$, $g_m/(WdL^{-1}) = \sim 3375\text{ S/m}$).^[9]

Figure 2. (a) Schematic diagram of the OEET. (b) Output characteristics for V_G varying from -0.2V (top curve) to 0.6V (bottom curve) with step of + 0.2V. The inset shows the optical micrograph of the patterned channel. Scale bar, 200 μm . (c) Transfer curve for $V_D = -0.5\text{V}$, and the associated transconductance (g_m). The time delay was 200 ms. (d) Scaling of OEET transconductance with channel geometry where transconductance (g_m) at saturation ($V_G = 0.3\text{V}$) is plotted as a function of WdL^{-1} , and V_D that corresponds to saturation. The line shows a linear fit ($R^2 = 0.94$) as predicted from equation (1).

To delve into the doping mechanism and examine whether the exchange of counterion has an impact on PEDOT:PSS states upon reduction, the change in optical absorption spectra of the films immersed in the electrolyte under biasing was monitored (**Figure 3**). The films are cast on ITO-coated substrates and the UV-vis-NIR spectra were acquired at increasing positive voltages applied on the Ag/AgCl pellet electrode. A comparative study using pristine PEDOT:PSS has also been conducted. As shown in Figure 3(b), the spectrum of pristine PEDOT:PSS displays a band at about 970 nm that is ascribed to polaron absorption, and the absorption spectrums above 970 nm are attributed to bipolaron PEDOT^{2+} .^[34] Upon application of positive voltages, the PEDOT:PSS film switches from oxidized to neutral state

since the injected cations from the electrolyte de-dope the PEDOT. As a result, the recorded spectrum showed the emergence of a band at 645nm which is attributed to the π - π^* transition of neutral or de-doped PEDOT. When the potential E is increased to +0.8V, the intensity of the polaronic and bipolaronic optical transitions at near IR region reduced significantly. This is consistent with the transition of PEDOT chains from the bipolaron (PEDOT^{2+}) to polaron (PEDOT^+) and neutral (PEDOT^0) states.^[34,37] In strong contrast, the spectrum recorded for PEDOT:PSS/[EMIM][TCM] biased at $E = +0.8\text{V}$ shows that the film still has relatively high absorption at near IR transitions, which points that charged polarons are still present in PEDOT:PSS/[EMIM][TCM] film. This suggests that higher biasing is needed to reduce the composite film completely compared to that of pristine PEDOT:PSS film. This effect suggests that there is a strong level of interaction between [EMIM][TCM] and PEDOT:PSS; a significant amount of TCM anions remain in the PEDOT phases (as PEDOT:TCM), even after the rinsing, and induce additional p-doping in PEDOT. 1000 cycles were also performed, where the bias voltage switches from -0.4V to 0.6V, and the absorption feature of [EMIM] in the UV range ($\sim 340\text{nm}$) remained over the course of the biasing operations (see Figure S3, Supporting information), further providing evidence that the ionic liquid component remains in the polymer film. Absorption changes also have been recorded at fixed 900 nm wavelength while switching the potentials from $E = +0.75\text{V}$ to 0V or to -0.75V and vice versa (Figure 3(d)). The switching behaviour is similar to that of standard EG-modified PEDOT:PSS film (Figure S4, Supporting Information). No signs of absorption loss were observed during the cycling, indicating the PEDOT:TCM complexes did not undergo any degradation processes.

Figure 3. (a) Schematic of the setup for UV-vis measurement. UV-vis-NIR spectroelectrochemical data from $E = 0\text{V}$ to $+0.8\text{V}$ for (b) Pristine PEDOT:PSS and (c) PEDOT:PSS/[EMIM][TCM] in 100 mM NaCl electrolyte. (d) Time-resolved absorption of PEDOT:PSS/[EMIM][TCM] film in 0.1 M NaCl electrolyte at 900 nm wavelength, showing optical switching behaviour for applied voltages of $E = +0.75, 0, 0.75$, and -0.75V for 60s each.

According to equation (1) and measured g_m , we obtained a high μC^* value of $335\text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$, which is nearly four-order of magnitude higher than the control PEDOT:PSS device (Figure S5, $0.03\text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$) and compares favourably against all OECT materials ($\mu C^* \sim 0.1 - 228\text{ Fcm}^{-1}\text{V}^{-1}\text{s}^{-1}$).^[14] Electrochemical impedance spectroscopy measurements were carried out to determine the volumetric capacitance independently. The impedance results are fitted to an equivalent RC circuit model; $R_s(R_p || C)$ where R_s is the resistance of the electrolyte, C and R_p represent the capacitance and resistance of the PEDOT:PSS based films, respectively (Figure S6, Supporting Information). The volumetric capacitance C^* is then determined by using the C term extracted from the circuit model and normalized with

the volume of the film (**Figure 4(a)** and Figure S6). In general, the volumetric capacitance is high, exhibiting an average C^* of $37 \pm 2 \text{ F cm}^{-3}$ (with 0.5 wt.% [EMIM][TCM]), $59 \pm 5 \text{ F cm}^{-3}$ (with 1 wt.% [EMIM][TCM]) and $87 \pm 5 \text{ F cm}^{-3}$ (with 1.5 wt.% [EMIM][TCM]), which is an indication of enhanced ionic transport with increasing concentration of ionic liquid. These C^* values were also found to be higher when compared to that of EG-modified PEDOT:PSS ($\sim 40 \text{ F cm}^{-3}$).^[38] Since the g_m is determined by the product of μ and C^* , the hole mobility of the films was also estimated to be $3.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

The high μ and C^* implies the existence of an efficient pathway for carrier transport as well as effective ion injection/penetration. As evident in the TEM images in Figure 4(b), the counter-ion exchange can influence the composition and thus film morphology, where an interconnected network of fibrillar structure in PEDOT:PSS/[EMIM][TCM] with better connectivity was observed. This is in contrast to the typical granular structure in pristine PEDOT:PSS film. Due to the strong affinity of ionic liquids with conductive polymers, it is likely that the TCM anions disrupt the PEDOT:PSS attraction and bring the PEDOT chains together to form the fibrillar morphology and thus allows an efficient pathway for hole transport.^[22] The high aspect ratio of the fibrillar network can also allow more interfacial and surface area for ion penetration and dedoping/doping to occur.

The structural changes and π - π stacking distances have been further examined using grazing-incidence wide-angle x-ray scattering (GIWAXS).^[39] Figure 4(c) presents the 2D GIWAXS data and the 1D q_z profiles extracted from the 2D raw detector patterns in q -space are shown in Figure 4(d). In the case of pristine PEDOT:PSS, the stacking of PSS is seen at $q_z = 1.23 \text{ \AA}^{-1}$ ($d = 5.11 \text{ \AA}$) and the π - π stacking of PEDOT (010) is observed at $q_z = 1.73 \text{ \AA}^{-1}$ ($d = 3.63 \text{ \AA}$). A weak ring at $0.29 \text{ \AA}^{-1}$ ($d = 21.7 \text{ \AA}$) indicates lamellarly stacked PEDOT and PSS molecules in all directions but dominantly in the vertical direction. Contrastingly, for PEDOT:PSS/[EMIM][TCM], the stacking feature of PEDOT and PSS becomes less well

defined for the mixed material, possibly due to the removal of PSS upon ionic liquid doping. The dominant change upon ionic liquid doping is a significantly enhanced PEDOT stacking with a reduced lattice spacing at $q_z=1.77 \text{ \AA}^{-1}$ ($d= 3.55 \text{ \AA}$), as indicated by the more pronounced (010) Bragg reflection. Therefore, the design of this PEDOT:PSS/[EMIM][TCM] can serve to induce higher and more closely packed order of PEDOT units and interconnected network of fibrillar structure to enhance its mobility and volumetric capacitance simultaneously.

Figure 4. (a) Volumetric capacitance ($V=0.5V$) of PEDOT:PSS films with different concentration of [EMIM][TCM]. (b) Bright-field TEM images of PEDOT:PSS films with and without [EMIM][TCM]. The scale bar represents 200nm. (c) 2D GIWAXS data of PEDOT:PSS films with and without [EMIM][TCM] (d) 1D scattering profile in the out of plane direction. (e) Transient response of drain current for a constant $V_D = -0.5V$ and 0.8V pulse applied at the gate. The solid red line is an exponential fit with a rise time of 3.9 ms. (f) Transient response of drain current with V_G switches from 0.8V to -0.4V for pulse width of 0.5 s, and constant $V_D = -0.5V$ for 500 cycling pulses.

The response time is a function of how fast the ions penetrate into the polymer channel and extraction of charge carriers at the source/drain contacts. Although the μC^* product is a steady-state parameter, the high volumetric doping within the channel is a good implication of effective ion penetration/transport and should translate to good response time in the OEET.^[14] In this work, the response time of the OEET is determined to be 3.9 msec (**Figure 4(e)**), faster than the control device (pristine PEDOT:PSS, 30 msec, Figure S5) for a

channel thickness of 200 nm, which clearly indicates the effectiveness of the ion penetration in the PEDOT:PSS/[EMIM][TCM] channel. A faster response can be further attained by making the channel thinner since the dedoping requires a smaller number of ions.^[29] In addition, Figure 4(f) presents the cycling stability of the device, where successive gate voltage pulses are applied (with V_G switches from 0.8V to -0.4V for a pulse width of 0.5 s, and constant $V_D = -0.5V$). The PEDOT:PSS/[EMIM][TCM] channel exhibits high switching stability, where the drain current (I_D) retained 93 % of the original value after 500 cycles. Similarly, thicker films ($d \sim 400\text{nm}$) of PEDOT:PSS/[EMIM][TCM] exhibit high switching stability under 3600 cycles (see Figure S7, Supporting Information). Furthermore, devices stored in air for over one month showed little decline in performance (Figure S8).

OEET is particularly attractive for sensing applications since the high g_m translates to high sensitivity.^[29] The detection and quantification of ionic species in aqueous media and in particular, biologically relevant ions (K^+ , Na^+ , Ca^{2+}), is of importance to several fields such as environmental monitoring, health diagnostics, water and food test.^[7,40] We thus utilized the ionic liquid doped PEDOT:PSS OEET to detect Na^+ in water and studied its ion-sensitive behavior. The inset of Figure 5(a) shows the circuit configuration of the OEET in ion-sensing mode with a bias current I_D set by the current source. Under the ion-sensing mode, an input signal V_I is applied at the gate, and the output voltage V_O dropped across the current source is evaluated. The output voltage V_O has two prominent distinct features corresponding to the linear and saturation regimes of the transistor. When the ion concentration is changed, the minimum V_I (assigned as V_{SW}) required to switch the transistor from linear to saturation mode is also changed thereby making it sensitive to the ion concentration, c . In our experiments, the ion sensitivity is evaluated for concentration as low as 0.01 M to as high as 1 M. By increasing c , the switching voltage shifts towards negative voltage. For instance, at $c = 1$ M, $V_{SW} = 0.33$ V while at $c = 0.1$ M, $V_{SW} = 0.51$ V. Thus, the V_{SW} shifts to lower positive

voltages when the ion concentration is increased. It is possible to shift V_{SW} back within the supply voltage range by increasing the current bias I_D (Figure 5(a)).^[41] This allows both high sensitivity and low voltage operation. To investigate the ion sensitivity of the current-driven OECTs, we evaluate the cumulative shift of the switching voltage V_{SW} under different ion concentrations (Figure 5(b)), which was defined as $\Delta V_{SWi+1} = \Delta V_{SWi} + (V_{SWi+1} - V_{SWi})$, with a bias current $I_D = -1$ mA. Figure 5(c) shows the measured V_{SW} as functions of ion concentration. From the linear approximation of all the measured V_{SW} , the ion sensitivity is about 146 mVdec^{-1} , which is much higher than the theoretical Nernstian sensitivity of 59.2 mVdec^{-1} . Higher ion sensitivity can be realised by reducing the channel dimensions.^[41] Further, we determine the lowest ion concentration detectable by the device through a change in channel resistance (ΔR_{DS}) to the various concentration of Na^+ solutions. Clearly, the change in channel resistance is discernible up to a concentration as low as $1 \text{ } \mu\text{M}$ corresponding to a ΔR_{DS} of $10 \text{ } \Omega$ (Figure 5(d)). It is worth mentioning that for concentrations lesser than $1 \text{ } \mu\text{M}$, ΔR_{DS} could also arise due to the H^+ doping of PEDOT:PSS.^[3]

Figure 5. (a) Current-driven transfer characteristics under various bias, varying from $I_D = -1\text{mA}$ (right, red curve) to $I_D = -2\text{mA}$ (left, grey curve) with a step of -0.5mA . (b) Current-driven transfer characteristics as a function of ion concentration, ranging from 0.01 M (right, black curve) to 1 M (left, cyan curve). (c) Cumulative switching voltage variation as a function of ion concentration. The ionic sensitivity of PEDOT:PSS/[EMIM][TCM] based OECT is $\sim 146\text{ mV dec}^{-1}$. (d) Change in channel resistance, ΔR_{DS} , as a function to various concentration of Na^+ solutions. Channel dimension: $W=1000\text{ }\mu\text{m}$, $L=100\text{ }\mu\text{m}$, and thickness $d=200\text{ nm}$.

In addition to presenting the OECT performance, the PEDOT:PSS/[EMIM][TCM] films were found to have good compatibility with mechanical flexible substrates and resistance to physical deformation. Here, the PEDOT:PSS/[EMIM][TCM] is directly coated onto hydrogenated styrene ethylene butylene styrene (SEBS) elastic substrates. We found that the composite films exhibit stretchable texture and can withstand strains up to 40% (Figure S9). This is in contrast to pristine PEDOT:PSS which is easily vulnerable to fracture under external strain ($< 5\%$ fracture strain). The improved stretchability of the PEDOT:PSS/[EMIM][TCM] film is likely due to the plasticizer effect of the ionic liquid and enhancing the segmental motion of the polymer chains, and thus provide a promising

application for flexible and stretchable electronic devices. Finally, we characterized OECTs with PEDOT:PSS/[EMIM][TCM] channel, having an effective thickness $d = \sim 800$ nm, on flexible polyarylate (PAR) substrate, (**Figure 6(a)** and (b)). The output and transfer characteristics of the flexible OECT are depicted in Figure 6(c) and (d). It exhibited a maximum transconductance of about 28.7 mS at $V_G = 0.42$ V, which is comparable to the rigid device performance. The flexible OECT can maintain a stable performance under a bending radius (R) of 11 mm, where the corresponding peak transconductance exhibits a slight variation after bending, indicating its robustness towards physical deformation. We have also measured the change of the lateral current flowing through the film when the substrates were bent to different radii ($R = 15, 10, 5$ mm). As shown in Figure S9, the current loss was only about 1% at the bending radius of 5 mm.

Figure 6. (a) Photograph, (b) bending test ($R = 11$ mm) of PEDOT:PSS/[EMIM][TCM] OECTs ($W = 1000$ μm , $L = 200$ μm) on flexible PAR substrate. (c) Output and (d) transfer characteristics for the flexible device before and after bending.

In conclusion, mixing ionic liquids with PEDOT:PSS is an efficient strategy to simultaneously maintain good electronic and ionic transport and is clearly reflected in the obtained high μC^* figure of merit ($\sim 335 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$). The ionic liquid inclusion reduces the interactions between the PSS groups and PEDOT chains to facilitate polymer movement and closely pack the PEDOT units together to form the fibrillar morphology. At the same time, there is enhanced ion penetration through the high aspect ratio of the fibrillar network. Consequently, the PEDOT:PSS/[EMIM][TCM] based OECT exhibits a record high transconductance of $\sim 7100 \text{ S/m}$ and fast transient response of 3.9 ms. The strong affinity of the ionic liquid with PEDOT:PSS also manifests as an increase in charged polarons and translates to a relatively high biasing ($V_G \sim 0.8 \text{ V}$) required for switching the OECT to off state. Since the applied voltage is limited to 1V for aqueous electrolyte to prevent electrolysis, the use of polyelectrolyte or ion gels can allow for higher voltage operation.^[9,42,43] For lower voltage operation, a promising avenue may be to examine ionic liquids with weaker ion-exchange reaction, while still enabling the favourable fibrillar morphology.

In addition to improving the electronic and ionic transport, the addition of ionic liquid is a simple way to enhance the flexibility and deformability of the OECTs by integrating its plasticising effect. The OECTs are further capable of having good ion sensitivity. Given the extensive library of ionic liquids, a new diversity of conducting polymers with tailored electronic and ionic transport as well as superior mechanical properties can be envisioned and is particularly relevant for many bioelectronics devices.

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Supporting Information

Ionic liquid doping enables high transconductance, fast response time and high ion sensitivity in organic electrochemical transistors

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Experimental Section

Materials: PEDOT:PSS (Clevios PH1000) was purchased from Heraeus and used as received in this work. PDMS (Sylgard 184) was purchased from Dow Corning Corp. Glycidoxypyriltrimethoxysilane (GOPS) were obtained from Sigma-Aldrich. The synthesis of [EMIM][TCM] was conducted according to previously reported procedures.^[1]

Films preparation: The PEDOT:PSS/[EMIM][TCM] composites were prepared by mixing 0.15 M [EMIM][TCM] (between 0.5 to 1.5wt% in deionized water) to PEDOT:PSS solution, and stirred vigorously for 10 min. A 0.5 vol.% of GOPS was added to the final solution and stirred overnight. The role of GOPS is to stabilise the PEDOT:PSS films in aqueous electrolyte. Pristine PEDOT:PSS mixed with 0.5 vol% GOPS were also prepared. The EG-modified PEDOT:PSS film was prepared as previously reported^[2] by adding 5 vol.% ethylene glycol (EG), 0.1 vol.% dodecyl benzene sulfonic acid (DBSA), and 0.5 vol.% of

GOPS into the PEDOT:PSS solution and sonicated before spin-coating. The thickness of the resultant films was carried out using an Alpha-Step profilometer (KLA-Tencor).

OECTs Fabrication: The OECTs were fabricated on the silicon wafers. The silicon substrates were first cleaned by sonication in soap water, deionized water, acetone and ethanol for 10 min successively, followed by drying with nitrogen. The patterning method for OECT channel is followed according to the previous report.^[3] In brief, a thin layer of poly(methylmethacrylate) (PMMA) [Polysciences, Inc., $M_w=100,000$] (5 wt.% in toluene) was spin-coated on the cleaned substrates at 4000 rpm for 30s. The PMMA film was then irradiated with ultraviolet-ozone (UVO) (Model No. 18-220, Jelight Company, Inc.) through a shadow mask for one hour, followed by rinsing with deionized water to remove residual PMMA in the patterned area ($1000\ \mu\text{m} \times 500\ \mu\text{m}$). The patterned PMMA were then treated with UVO for another 10 min. The PEDOT:PSS/[EMIM][TCM] solution was spin coated onto the patterned PMMA substrates at various spin-speed to achieve different thickness, followed by annealing at $130\ ^\circ\text{C}$ for 1h. After that, the sacrificial PMMA layer were removed by dipping the sample into toluene for 10 s and rinsed with deionized water. The gold source and drain contacts (thickness of 100 nm) were evaporated through a shadow mask. All the active PEDOT:PSS films were rinsed with deionized water before any characterization to remove small molecules on the surface. The poly(dimethylsiloxane) (PDMS) was used to confine the electrolyte. PDMS was mixed at a ratio of 10:1 (base to cross-linker) and cured at $80\ ^\circ\text{C}$ for 4h. After that, a small PDMS well ($8\ \text{mm length} \times 8\ \text{mm width}$) was cut and fixed on top of the channel by epoxy glue, followed by curing the epoxy under UV light for 2 min. For the strain test, the PEDOT:PSS films were casted on elastic polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SEBS) elastomer (with 20% styrene content, Turtec H1052, supplied by AK Elastomer). The SEBS substrate was prepared from a toluene solution (300mg/ml) casted onto a glass slide. For flexible devices, the same device

fabrication processes are done on polyarylate (PAR) substrate (Ferranias Arylite[®]).

Electrical characterization: The output and transfer characteristics of the OECT were measured under ambient in the dark at room temperature using a Keysight precision source/measure unit (B2900A Series) and a probe station (Karl Suss PM5). The devices operated in the common source configuration. The electrolyte was a 0.1M NaCl solution and dropped into the PDMS well. The gate electrode was a Ag/AgCl pellet and immersed in the electrolyte. The conductivity of the PEDOT:PSS/[EMIM][TCM] films were measured by four-point probe station (AIT, CMT-SR2000N), with at least 10 regions measured and averaged.

GIWAXS: The samples for GIWAXS measurements were prepared by spin-coating the respective solution on silicon substrates and annealing at 130 °C for 1h. All the substrates were rigorously rinsed by DI water and blow dried using N₂ before annealing at 100 °C for 10 minutes. GIWAXS measurements on thin films were carried out under vacuum on the Ganesha 300XL SAXS-WAXS system with an operating wavelength of 1.5406 Å. An incidence angle of 0.2° was employed, which is near the critical angle of the silicon substrates to keep a constant irradiated volume. GIWAXS data was recorded on a Pilatus 300k area detector, maintaining a sample-detector distance (SDD) around 106 mm. GIXSGUI was used to treat GIWAXS data and do all necessary corrections.^[4]

FTIR: FTIR measurements were done on a JASCO-FT/IR-6700 instrument, in transmission mode. The samples for FTIR measurements were prepared by drop-casting the respective solutions on glass substrates and left to dry at room temperature for 12 hours.

TEM: TEM measurement (JEM-1400, JEOL, Japan) was performed to check the morphology of the resultant films. To prepare the TEM samples, the active layers were spin-cast on glass substrates, followed by submerging in deionized water and floated onto the air/water interface. The films were then picked up onto unsupported 300 mesh copper grids.

UV-vis Spectroelectrochemistry: The pristine PEDOT:PSS or PEDOT:PSS/[EMIM][TCM] solution was spin-coated on ITO glass substrates and subsequently annealed at 130°C for 1h. After that, care was taken to confine an 8 mm × 5 mm active area (PEDOT:PSS films). The PEDOT:PSS-coated ITO glass was immersed into a cuvette of 0.1M NaCl solution along with Ag/AgCl pellet as the gate electrode. A Keysight precision source/measure unit (B2912A) was chosen to apply biasing between Ag/AgCl pellet and ITO glass. The absorption spectra of the film was recorded using a UV-vis-NIR spectrophotometer (SHIMADZU, UV-3600) over the wavelength range from 300 to 1300 nm as sample was biased. The same spectrophotometer is used to record the absorption spectra of the films coated from pristine PEDOT:PSS and PEDOT:PSS containing different concentrations of [EMIM][TCM] on quartz substrates.

Impedance Spectroscopy: Impedance spectroscopy measurements (Autolab PGSTAT 128N) using three-terminal configuration were performed to determinate the capacitance. A micro-scale film patterned on top of Au electrodes was used as the working electrode, with Pt mesh and standard Ag/AgCl wire as counter and reference electrode, respectively. The measurement was performed in 0.1M NaCl aqueous electrolyte with an AC amplitude of 10mV.

Figure S1. UV-Vis spectrums of PEDOT:PSS-based films with and without [EMIM][TCM].

Figure S2. Double sweeping of (a) transfer and (b) output characteristics, showing negligible hysteresis in PEDOT:PSS/[EMIM][TCM]-based OECT ($W/L = 1000 \mu\text{m}/100 \mu\text{m}$, $d \sim 400 \text{ nm}$ thick).

Figure S3. (a) UV-vis-NIR absorption spectra of pristine PEDOT:PSS and PEDOT:PSS/EMIM TCM film (immerse in NaCl electrolyte) before ($E=0V$) and after 1000 cycles from $E = -0.4V$ to $0.6V$.

Figure S4. Time-resolved absorption of standard EG-modified PEDOT:PSS film in 0.1 M NaCl electrolyte at 900 nm wavelength, showing optical switching behaviour for pulses at $E = +0.75, 0, 0.75$, and $-0.75V$ for 60s each.

Figure S5. Electrical characteristics of pristine PEDOT:PSS based OECT ($W/L = 1000 \mu\text{m}/100 \mu\text{m}$, $d = 200 \text{ nm}$ thick) (a) Output characteristics for V_G varying from -0.6V (top curve) to 0.6V (bottom curve) with step of $+0.2\text{V}$. (b) Transfer curve for $V_D = -0.5\text{V}$, and the associated transconductance (g_m). The time delay was 200 ms . The extracted μC^* value, based on Equation (1), is $0.03 \text{ F cm}^{-1}\text{V}^{-1}\text{s}^{-1}$ at saturation region ($V_G = 0.3\text{V}$). (c) Transient response of drain current for a constant $V_D = -0.5\text{V}$ and 0.8V pulse applied at the gate for a pristine PEDOT:PSS based OECT. The red dashed line is an exponential fit with a rise time of 30 ms . (d) Electrochemical impedance spectroscopy (bode plots) for pristine PEDOT:PSS films. The modulus of the impedance, Z (black symbols), and phase (blue symbols) are plotted as a function of frequency. The results are fit to $R_s(C//R_P)$ equivalent circuit where R_s is the resistance of electrolyte, C and R_P represent the capacitance and resistance of the PEDOT:PSS films, respectively. Fits are shown as lines in light colors (Z fit, red; phase fit, grey). The area, thickness, R_s , C fit results are shown, as well as the resulting C^* value for the particular device.

Figure S6. Electrochemical impedance spectroscopy (bode plots) for PEDOT:PSS/[EMIM][TCM] films. The modulus of the impedance, Z (black symbols), and phase (blue symbols) are plotted as a function of frequency. The results are fit to $R_S(C//R_P)$ equivalent circuit where R_S is the resistance of electrolyte, C and R_P represent the capacitance and resistance of the PEDOT:PSS/[EMIM][TCM] films, respectively. Fits are shown as lines in light colors (Z fit, red; phase fit, grey). The area, thickness, R_S , C fit results are shown, as well as the resulting C^* value for the particular device. b) Capacitance of PEDOT:PSS films with 1.5 wt.% [EMIM][TCM] at different film volume. The linear fit ($R^2=0.98$) to the capacitance data yields a volumetric capacitance $87 \pm 5 \text{ F cm}^{-3}$.

Figure S7. Electrical characteristics of thicker PEDOT:PSS/[EMIM][TCM] OEET device ($W/L = 1000 \mu\text{m}/100 \mu\text{m}$, $d \sim 400 \text{ nm}$ thick), showing a higher transconductance ($g_m = 30.5 \text{ mS}$) and highly stable doping/dedoping process. (a) Output characteristics, (b) transfer characteristics for a drain voltage of -0.5 V . The transfer characteristics after undergoing 3600 cycles of pulse from -0.4 V to 0.6 V , with $V_D = -0.5 \text{ V}$ are also plotted for comparison. (c) Transient response of drain current for a constant $V_D = -0.5 \text{ V}$ and 0.6 V pulse applied at the gate. The red dashed line is an exponential fit with a rise time of 9.9 ms . (d) Stability study under a gate voltage pulse from -0.4 V to 0.6 V for more than 1 h (3600 cycles), with a drain voltage of -0.5 V .

Figure S8. Stability study of a PEDOT:PSS/[EMIM][TCM] based OEET ($W/L = 1000 \mu\text{m}/100 \mu\text{m}$, $d \sim 300 \text{ nm}$ thick). Transfer characteristics of a fresh OEET device (dotted line) and after storage in ambient conditions for one month (solid line), at a drain voltage of -0.5 V .

Figure S9. (a) Optical micrograph of PEDOT:PSS-based films with and without 1.5 wt.% [EMIM][TCM] under diverse strain. Scale bar, 200 μm . (b) Photograph of bending test on the PEDOT:PSS films on PAR substrate with gold electrodes. The distance between the electrodes is 200 μm . (c) Measured current versus bending radius. The inset shows the schematic of the bending test and the bending radius.

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