Supporting Information

Conjugated Polyelectrolytes as Water Processable Precursors to Aqueous Compatible Redox Active Polymers for Diverse Applications: Electrochromism, Charge Storage, and Biocompatible Organic Electronics

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Additional Experimental Details

Materials

ProDOT(EH)-EDOT and ProDOT(HD)-EDOT were prepared as previously reported.[1, 2] The dibromo-tetraester ProDOT monomer was prepared via a previously published method.[3] EDOT (97 %) was obtained from Alfa Aesar and vacuum distilled prior to use. $Pd(OAc)_2$ (98 %, Strem Chemicals), pivalic acid (99 %, Sigma), K_2CO_3 (anhydrous, Oakwood Products), 18-Crown-6 (99 %, Acros), diethyldithiocarbamic acid diethylammonium salt (97 %, TCI America), KOH (Technical Grade, Fisher Scientific), and pTSA (monohydrate, 98 %, Alfa Aesar) were used as received. DMAc (HPLC grade, Alfa Aesar) was filtered through a pad of alumina (basic, Sigma Aldrich) and degassed by argon bubbling prior to use. Sodium chloride (NaCl, biotechnology grade, Amresco) and lithium bis(trifluoromethanesulfonimide) (LiBTI, 99 %, Acros Organics) were used as received. Gatorade™ (Glacier Cherry) and Powerade™ (White Cherry) were purchased from a local grocery store and were degassed with argon. Propylene carbonate (PC, Acros Organics, 99.5 %) was purified using a solvent purification system built by Vacuum Atmospheres. Deionized (DI) water was collected by purification of tap water using a EMD Millipore Milli-Q Ultrapure Water system. Ringer's Solution (Amphibian, Lab Grade) and Human Serum (Normal) were purchased from Ward's Science and Atlanta Biologicals, respectively. Other solvents used (such as methanol, hexanes, and diethyl ether) were obtained from VWR and used as received except for chloroform,

which was obtained from BDH. The cellulose separator was a cut piece of filter paper (Qualitative, Fine, Fisher Scientific).

Instrumentation

The ^{1}H-NMR (64 scans) spectrum was collected on a Bruker ASCEND 800 MHz instrument using CD_2Cl_4 as a solvent at a temperature of 323K. The molecular weight and dispersity of the polymer were obtained using a THF GPC at 35°C calibrated vs. polystyrene standards. The electrochemical measurements on films were performed in a three-electrode cell setup using either a Ag/Ag^+ reference electrode (10 mM $AgNO_3$ in 0.5 M $TBAPF_6$-ACN, $E_{1/2}$ for ferrocene: 68 mV) for organic electrolytes or a Ag/AgCl reference electrode (1M KCl, purchased from CH Instruments, Inc.) for aqueous electrolytes, the counter electrode was a platinum flag. The cyclic voltammetry was performed on an EG&G PAR (model 273A) potentiostat/galvanostatic under CorrWare control. The long-term charge/discharge experiments on the Types I supercapacitor devices were performed on a Pine bipotentiostat (model AFCBP1) and monitored using AfterMath software. Galvanic cycling experiments were performed on a Metrohm Autolab Potentiostat/Galvanostat (Type PGSTAT101) and were monitored using NOVA 2.0 software. Spectroelectrochemistry and chronoabsorptiometry were measured using an Agilent Technologies Cary 5000 UV-Vis-NIR Spectrophotometer under Cary WinUV control and a EG&G PAR (model 263A) potentiostat/galvanostatic under CorrWare control.

Figure and Tables

Electrolyte	Conc. (M)	Conductance (mS/cm)
LiBTI/PC	0.5	2.98
LiBTI/H_2O	0.5	21.2
NaCl/H_2O	0.5	46.0
Ringer's	N/A	12.4
Human Serum	N/A	12.9
Powerade	N/A	2.81
Gatorade	N/A	2.12

Table S1: Conductance of various electrolytes

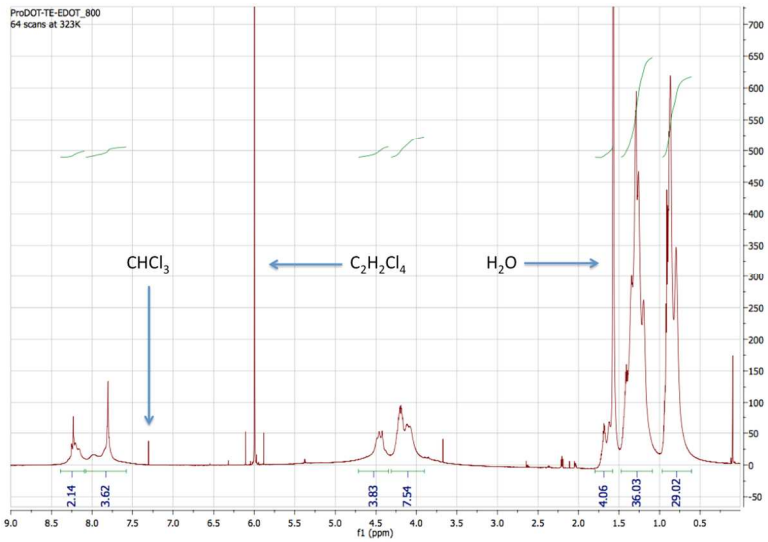

Figure S1: ^{1}H-NMR (800 MHz, CD_2Cl_4, 323K) of the OS-polymer (OS-PE).

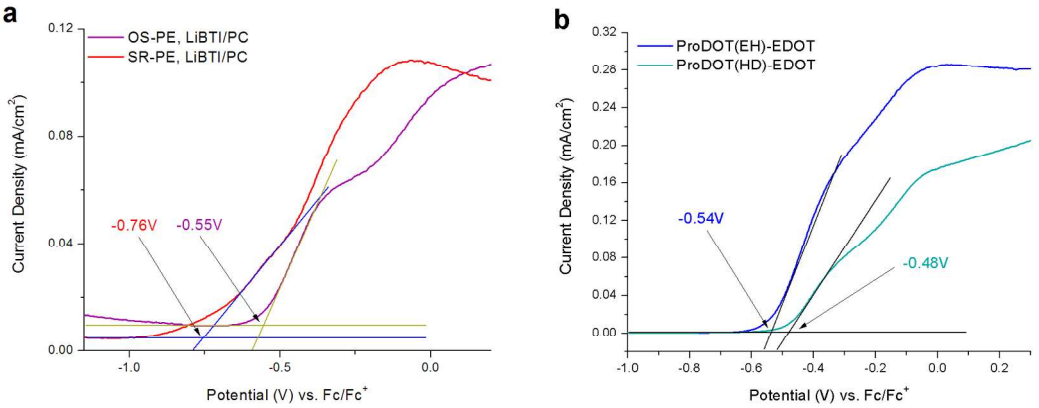

Figure S2: Differential pulse voltammetry curves of a) the OS-PE and SR-PE and b) the 2-ethylhexyl (ProDOT(EH)-EDOT) and 2-hexyldecyl (ProDOT(HD)-EDOT) functionalized polymers on glassy carbon electrodes in 0.5 M LiBTI/PC vs. Fc/Fc$^+$.

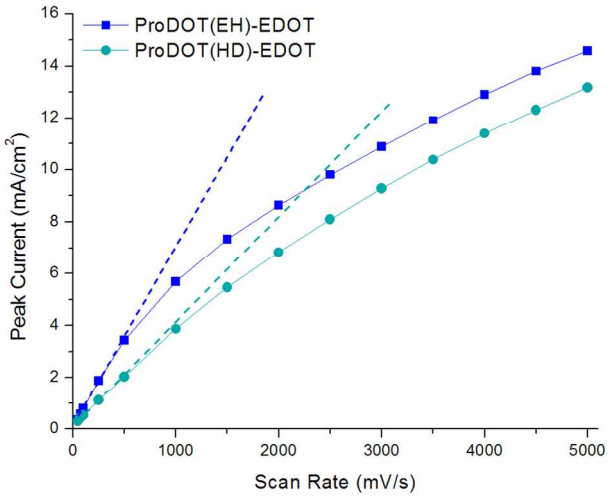

Figure S3: Scan rate dependences of drop-cast films of ProDOT(EH)-EDOT and ProDOT(HD)-EDOT on glassy carbon button electrodes in 0.5 M LiBTI/PC. Dashed lines illustrate the deviation from linearity at scan rates above 250 mV/s.

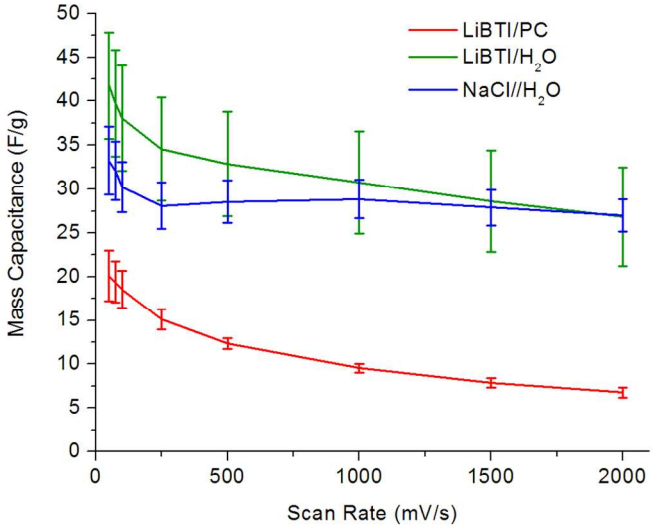

Figure S4: Mass capacitance (calculated from cyclic voltammograms) as a function of scan rate for films of SR-PE in various electrolytes.

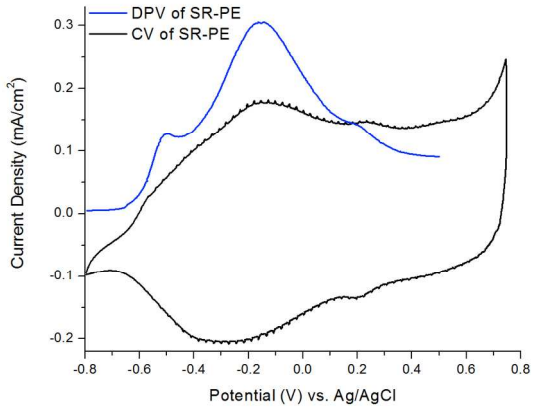

Figure S5: DPV and CV traces of the SR-PE polymer in 0.5 M LiBTI after protonation of the CPE using 1 M HCl/methanol.

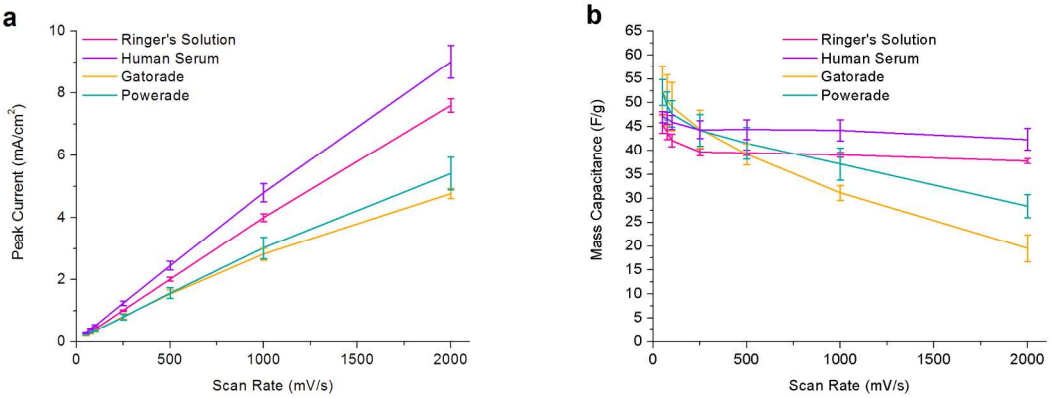

Figure S6: a) Peak current as a function of scan rate of SR-PE and b) mass capacitance as a function of scan rate of SR-PE films in various novel electrolytes.

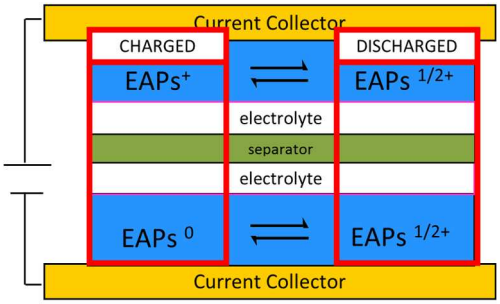

Figure S7: Schematic of a Type I supercapacitor in the charged state on the left and the discharged state on the right.

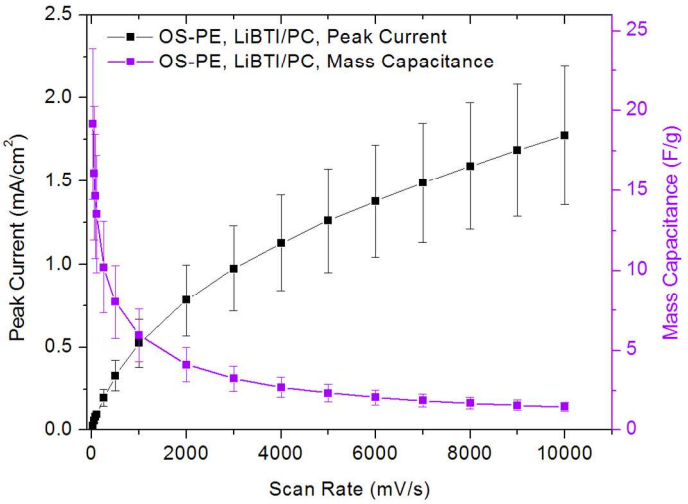

Figure S8: Peak current and mass capacitance as functions of scan rate for OS-PE devices with LiBTI/PC as the electrolyte.

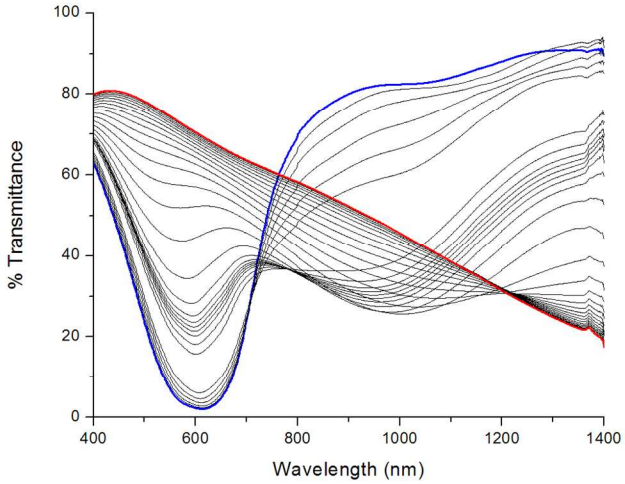

Figure S9: Transmittance spectra of the SR-PE in 0.5 M NaCl/H_2O at potentials (in 50 mV increments) from -0.80 to 0.70V vs Ag/AgCl.

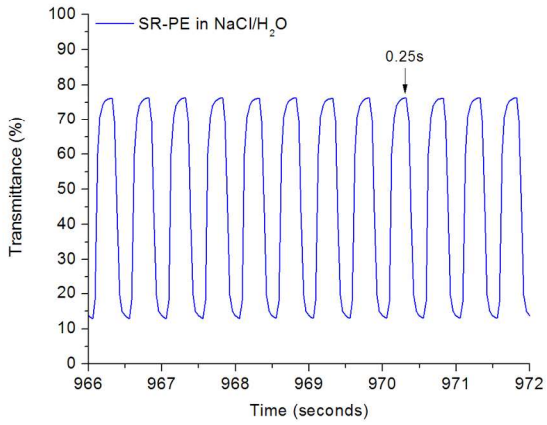

Figure S10: Chronoabsorptiometry (magnified) of the SR-PE on ITO glass in the $NaCl/H_2O$ electrolyte at 0.25 sec switching time.

$$g_m = \frac{Wd}{L}\mu C^*(V_T - V_G)$$

Equation S1: Transconductance (where: g_m is transconductance, W is the channel width, d is the channel thickness, L is the channel length, μ is the mobility of the active material, C^* is the volumetric capacitance of the active material, V_T is the geometry-independent threshold voltage, and V_G is the gate voltage).[4, 5]

1. J. A. Kerszulis, K. E. Johnson, M. Kuepfert, D. Khoshabo, A. L. Dyer and J. R. Reynolds, Tuning the painter's palette: subtle steric effects on spectra and colour in conjugated electrochromic polymers. *J. Mater. Chem. C* **2015**, *3*, 3211-3218.
2. J. F. Ponder, A. M. Österholm and J. R. Reynolds, Designing a Soluble PEDOT Analogue without Surfactants or Dispersants. *Macromolecules* **2016**, *49*, 2106-2111.
3. P. Shi, C. M. Amb, A. L. Dyer and J. R. Reynolds, Fast switching water processable electrochromic polymers. *ACS Appl. Mater. Interfaces* **2012**, *4*, 6512-6521.

4. J. Rivnay, P. Leleux, M. Ferro, M. Sessolo, A. Williamson, D. A. Koutsouras, D. Khodagholy, M. Ramuz, X. Strakosas, R. M. Owens, C. Benar, J.-M. Badier, C. Bernard and G. G. Malliaras, High-performance transistors for bioelectronics through tuning of channel thickness. *Sci. Adv.* **2015**, *1*, 1-5.
5. C. B. Nielsen, A. Giovannitti, D.-T. Sbircea, E. Bandiello, M. R. Niazi, D. A. Hanifi, M. Sessolo, A. Amassian, G. G. Malliaras, J. Rivnay and I. McCulloch, Molecular Design of Semiconducting Polymers for High-Performance Organic Electrochemical Transistors. *J. Am. Chem. Soc.* **2016**, *138*, 10252-10259.