A Side-Chain Defunctionalization Approach Yields a Polymer Electrochrome Spray-Processable from Water

By *Pierre M. Beaujuge*, *Chad M. Amb*, and *John R. Reynolds**

When compared to their inorganic counterparts (e.g., MoO_3, NiO_x), non-emissive organic electrochromics offer the potential for cost-effective solution processing over large-area and mechanically deformable surfaces. The ability to print discrete electrochromic pixels would pave the path to combining colors in portable display applications, such as information tags and electronic paper.[1–4] While a number of important design principles have been developed over the years to produce π-conjugated electrochromic polymers (ECPs) with varying color states and redox switching properties,[3] only a limited number of these electrochromes have shown print- or spray-processability from conventional organic solvents.[1,5–8] Attempts to print or spray thin films of neutral state ECPs from aqueous solvents have not been reported, likely due to a combination of solubility and film-forming challenges in polar media with relatively low vapor pressure. To date, only poly(3,4-ethylenedioxythiophene) (PEDOT), solution-cast in its heavily doped form PEDOT:PSS (polystyrene sulfonate), has been effectively processed from aqueous solutions.[9–12] Here, we report on the use of a side-chain defunctionalization approach in producing the first water spray-processable π-conjugated polymer electrochrome. The ability to spray-process ECPs from aqueous media is expected to minimize environmental impact and processing costs, hence promoting the commercial viability of this fast-developing technology suitable for flexible display applications.[3,4,13]

In comparison with liquid-crystal and light-emitting display technologies, non-emissive electrochromic systems benefit from being practical under a wide range of viewing directions and lighting intensities, such as direct sunlight. Their integration in low-drive-voltage powered information panels and tags, smart windows and mirrors, and in portable and shape-conforming operating systems including electronic paper, constitutes a focus of electrochromic device (ECD) development.[4]

Considering organic electrochromes for display device applications, the conjunction of synthetic accessibility, long-term redox stability, solution processability, and film-forming properties not attainable with small molecules, represent some of the many variables motivating the use of π-conjugated electroactive polymers. Beyond the synthetic accessibility, the ability to achieve palettes of colors by inducing simple changes in polymer repeat unit structures makes π-conjugated systems stand out over metal oxides. In this respect, extensive research effort is presently being invested in tailoring the complex interplay between molecular structure and optical absorption in systems exhibiting important spectral changes in their successive redox states.[3] In parallel, the development of sustainable solution-processing approaches adapted to low-cost, ambient, non-toxic, and high-throughput manufacturing conditions could rapidly take polymeric electrochromes to the forefront of the stage of organic electronics with commercial applicability.

Since the discovery of electrochromic effects in substituted and unsubstituted polythiophenes,[14–17] a library of thiophene- and pyrrole-containing π-conjugated electrochromic hybrids reflecting or transmitting distinct colors upon electrochemical doping has been continuously implemented to span essentially all the useful colors needed for a display device.[3,18] While multichromic polymers could ultimately find use in configurations where the various color states attainable upon redox switching match the color requirements specific to the application being considered, the ability to turn colors "on" and "off" appears to be even more critical. In this respect, the off state of an electrochrome can be attained when a transmissive and colorless redox state is accessible, e.g., when the visible absorption of the chromophore can be fully depleted and transferred into the near-IR, allowing a device to transmit all visible colors.

In spite of the breadth of recent progress in the synthesis and characterization of π-conjugated polymer electrochromes with particularly desirable color states, examples of cathodically and anodically coloring polymers (switching between colored and transmissive states) are substantially sparser than those of multichromic derivatives.[3] Likely the most established cathodically coloring systems reported to date, poly(dioxythiophene)s such as PEDOTs and poly(3,4-propylenedioxythiophene)s (PProDOTs) can be easily oxidized from their neutral purple-blue-colored states to a highly transmissive doped state, owing to their high-lying highest occupied molecular orbitals (HOMOs).[19,20] While a number of strategies have initially been developed to produce and electrochemically characterize solution-processable PEDOTs,[21–23] the synthetic accessibility and environmental stability of their PProDOT counterparts have rapidly made these functional polymers a mainstay of electrochromic polymer development.[6,24–29] In parallel, motivated by the need to implement and fine-tune colors, a number of spectral engineering principles have been developed in recent years in the field of π-conjugated organic polymers. For example, within the toolbox for spectral engineering, the donor-acceptor approach, alternating electron-rich and electron-deficient moieties along a π-conjugated backbone, has produced dual-band and broadly absorbing chromophores with neutral color states commonly difficult to achieve in π-conjugated polymers, such as

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[*] Dr. P. M. Beaujuge, Dr. C. M. Amb, Prof. J. R. Reynolds
The George and Josephine Butler Polymer Research Laboratory
Department of Chemistry
Center for Macromolecular Science and Engineering
University of Florida
Gainesville, FL, 32611 (USA)
E-mail: reynolds@chem.ufl.edu

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blue-green, green, and black for the most recent instances.[1,5,30–33] Building on this approach, we have recently described a blue-to-highly-transmissive switching polymer electrochrome with cleavable solubilizing side chains as an alternative to PEDOT.[8] In this work, the substitution pattern of the polymer was chemically removed in a post-deposition processing step to produce an electrochromic thin-film insoluble in conventional organic solvents,[34] hence suggesting a solution for the fabrication of long-lived electrolyte-based switchable devices.

Inspired by the success of this defunctionalization approach whereby cleaving the polymer solubilizing groups reveals new functionalities in close proximity to the π-conjugated backbone, we hypothesized that our methodology could be applied to the development of ionic π-conjugated polymer salts largely soluble in water and other polar protic aqueous mixtures. Ideally, the resulting polyionic intermediate could be solution-processed from the same aqueous solutions without the need to resort to any flammable and/or environmentally harmful organic solvents. While a number of sulfonated poly(dioxythiophene)s have been reported in the past,[35–37] their application has been limited to layer-by-layer depositions with non-electrochromic and inversely charged polymer counterparts, likely due to their solubility limits in aqueous media.

Here, using a simple homopolymer of 3,4-propylendioxythiophene (ProDOT) as a platform test, π-conjugated polymer electrochromes bearing alkyl ester side-chains are chemically synthesized and subsequently defunctionalized to yield polycarboxylate salts with low aliphatic content that are readily soluble in water and further spray-processable from water. Upon subsequent neutralization of the spray-cast thin-films, the electrochromic properties of the defunctionalized PProDOT are fully recovered and even enhanced in comparison to those of the substituted polymer precursor only processable from organic solvents. The resulting thin-film electrochrome is insoluble in common organic and aqueous solvents, introducing the perspective for the solution-deposition and superimposition of multiple electrochromic layers in vertically stacked ECDs.

Figure 1a describes the preparation of the dodecylester-substituted monomer precursor (**5**) to the organic solvent-processable PProDOT-ester (**6**); full synthetic details are reported in the Supporting Information. As described in Figure 1b, the PProDOT-ester produced on $FeCl_3$-mediated chemical oxidation of **5**, is subsequently neutralized using the reducing agent hydrazine and then washed with methanol (MeOH) before being extracted from chloroform ($CHCl_3$) according to conventional Soxhlet conditions. Following precipitation into MeOH, a fiber-like polymer suspension of PProDOT-ester is collected and dried, and can either be redissolved in organic solvents such as toluene to be spray-processed (traditional), or can be subjected to a side-chain defunctionalization protocol allowing transfer to an aqueous phase subsequently used for the solution-processing (non-traditional). In this second instance, the π-conjugated electrochrome is suspended in a 2 M solution of KOH in MeOH. The polymer suspension is stirred and refluxed for one day to yield a fine powder of PProDOT-salt (**7**), insoluble in MeOH, toluene, and $CHCl_3$, for example, but highly soluble in water at room temperature. The polycarboxylate salt **7** is dissolved in water (2 mg mL^{-1}) and the resulting solution is filtered and spray-cast onto ITO-coated glass slides using high-pressure argon (50–60 psi) and low solution flow rates at room temperature to achieve homogeneous films of varying thicknesses. The deposited films are finally neutralized by immersion for a few minutes in a MeOH solution of 0.1 wt% *p*-toluenesulfonic acid (*p*TSA) to yield the PProDOT-acid (**8**).

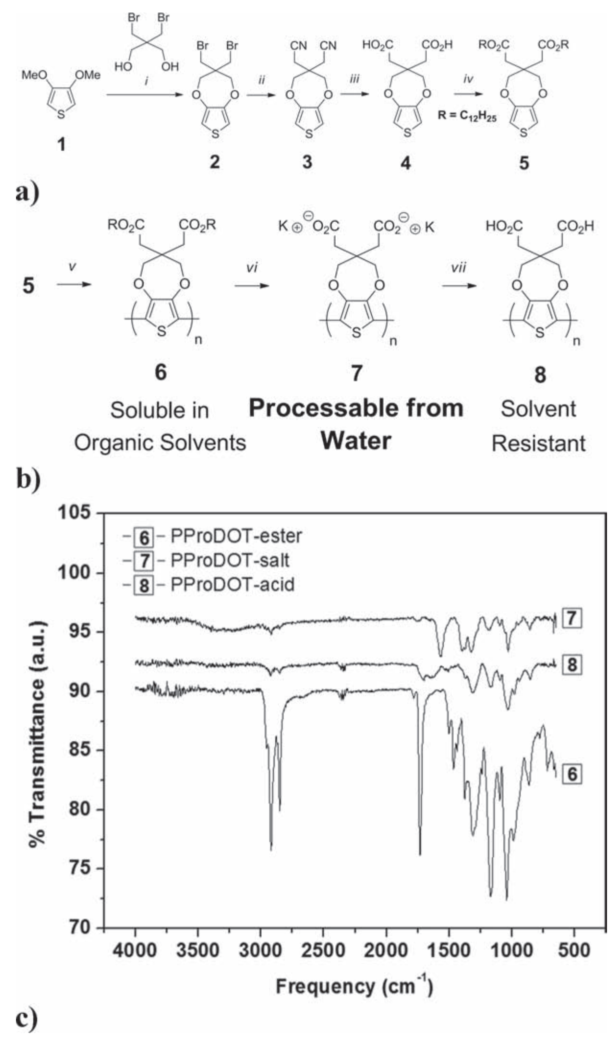

Figure 1. Polymer synthesis and side-chain defunctionalization. **a**) Monomer synthesis: *i*. *p*TSA (*para*-toluenesulfonic acid), toluene, 110 °C, 24 h; *ii*. NaCN, dimethyl sulfoxide (DMSO), 32 °C, 10 days; *iii*. KOH, ethylene glycol, water, 95 °C, 12 h; *iv*. dodecanol, EDCI (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide), DMAP (4-dimethylaminopyridine), CH_2Cl_2, 6 h. **b**) Polymer synthesis, side-chain defunctionalization, and neutralization: *v*. $FeCl_3$, $CHCl_3$, $MeNO_2$, 16 h; *vi*. KOH, MeOH, reflux, 24 h; *vii*. *p*TSA, MeOH, 2 min. **c**) ATR-IR spectra of a pristine film of PProDOT-ester spray-cast from toluene (**6**), of a film of PProDOT-salt spray-cast from water (**7**), and of a film of PProDOT-acid obtained on protonation (**8**).

The defunctionalization process was monitored by attenuated total reflectance infrared (ATR-IR) spectroscopy and the results are shown in Figure 1c. Here, the conversion from the ester-derivatized polymer electrochrome **6** to its polycarboxylate salt **7** is evidenced by a distinct shift of the C=O stretching band to lower frequency (from ca. 1730 to 1570 cm^{-1}) and a broadening of the same band. In addition, the clear decrease in C–H stretch intensity in the 3200–2800 cm^{-1} region upon going from **6** to **7** indicates the loss of the aliphatic solubilizing side chains. Upon protonation of the carboxylates, that is upon going from **7** to **8**, the C=O stretch shifts back to higher frequencies (ca. 1650–1710 cm^{-1}) and takes a bimodal structure. While the higher frequency peak (1710 cm^{-1}) corresponds to a fully protonated carboxylic acid functionality, the lower frequency peak (1650 cm^{-1}) is tentatively attributed to a pair of carboxylate moieties sharing the same proton.

A film of PProDOT-ester (absorption maximum = 0.87 a.u.) and a film of PProDOT-salt (absorption maximum = 1.2 a.u.) were spray-cast onto ITO-coated glass from toluene and water (both 2 mg mL^{-1}), respectively. **Figure 2a** provides clear evidence that concentrated water solutions of PProDOT-salt can be made and simply processed using a conventional air-brush. The film of PProDOT-salt was neutralized as described earlier in this manuscript to yield an insoluble film of PProDOT-acid. Both films were redox cycled until a stable and reproducible electrochemical switch was reached. Electrochemical oxidation of PProDOT-ester was carried out in 0.2 M lithium bis(trifluoromethylsulfonyl)imide (LiBTI)/propylene carbonate (PC) supporting electrolyte using a Ag/Ag$^+$ reference electrode and a platinum wire as the counter electrode. In contrast, electrochemical oxidation of PProDOT-acid was carried out in 0.2 M NaCl/water supporting electrolyte using a Ag/AgCl reference electrode, an electrolyte solution that did not allow the electrochemical switching of its PProDOT-ester precursor (hence confirming a change in solvent affinity on cleaving the polymer side-chains). As shown by the spectro-electrochemical experiments presented in Figure 2, the visible absorption of both systems (in red) bleaches extensively with increasing applied potential and this depletion is accompanied by the formation of polaronic and bipolaronic transitions in the near-IR. Once fully doped, only residual absorption can be detected in the 400–700 nm range (in blue), as expected for a colored-to-transmissive switching polymer electrochrome. In both cases, the onset of oxidation is consistent with the low values estimated at –0.37 V versus Fc/Fc$^+$ and –0.23 V versus Ag/AgCl via cyclic and differential-pulse voltammetry, respectively (see Figures S1,S2 in the Supporting Information). Determined from the onset of absorption of the solid thin films, the bandgap of the polymers remain relatively constant and on the order of 1.8 eV. Upon going from the colored neutral state to the transmissive oxidized state, a transmittance change on the order of 60% is estimated considering the maximum of absorption as a reference. The color states attained in each configuration are shown as insets in Figure 2b,c. Here, it can be seen that the defunctionalization process does not significantly alter the neutral state purple-blue of the electrochrome, which is in good agreement with the nearly identical neutral absorption spectra of the two films (except the vibronic features appear expectedly more pronounced in PProDOT-acid thin-films). Importantly, no appreciable difference in transmissivity is observed between the doped state of the PProDOT-ester and that of the PProDOT-acid; both achieve a remarkably high level of transparency when fully oxidized.

The large optical contrasts anticipated from spectro-electrochemical analysis and the particularly high level of transmissivity retained by the water-processed PProDOT analog were confirmed by monitoring the transmittance of the spray-cast

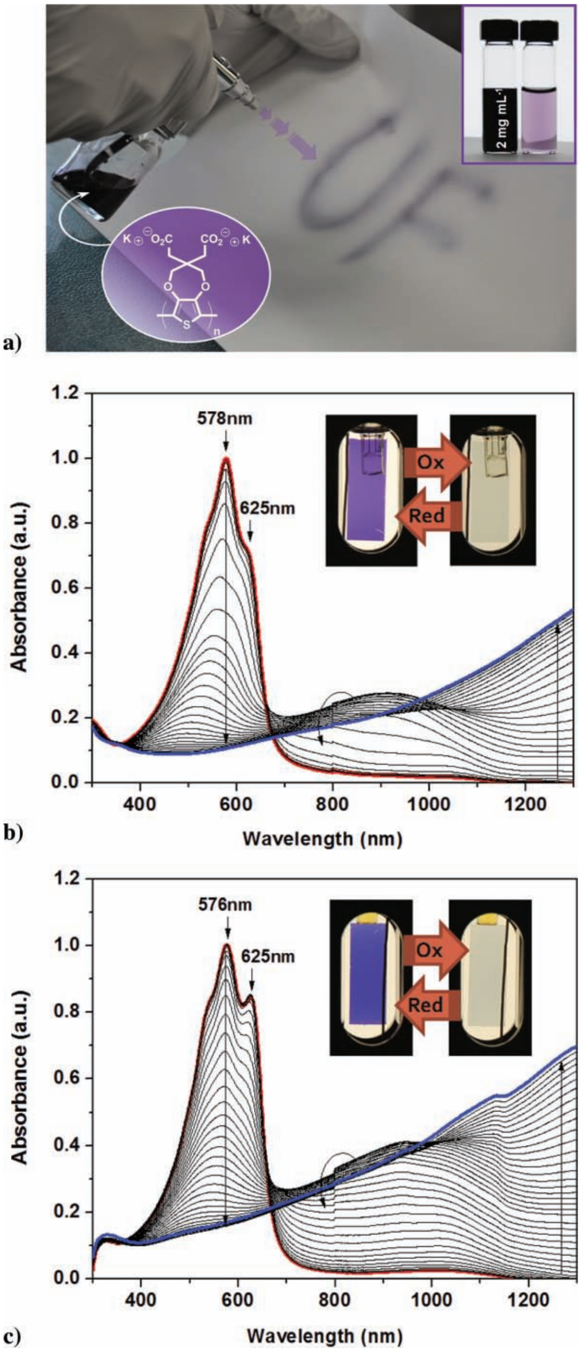

Figure 2. Polymer spectro-electrochemical comparative analysis. a) Concentrated water solutions of PProDOT-salt are made and simply processed using a conventional air-brush. b) Spectro-electrochemistry of PProDOT-ester (normalized at the polymer absorption maximum). The film was spray-cast onto ITO-coated glass from a toluene solution (2 mg mL^{-1}). The applied potential was increased in 25 mV steps: –0.47 to +0.46 V vs Fc/Fc$^+$. c) Spectro-electrochemistry of PProDOT-acid (normalized at the polymer absorption maximum). The film was spray-cast onto ITO-coated glass from a water solution of PProDOT-salt (2 mg mL^{-1}) and the deposited polyionic salt was neutralized by immersion in a MeOH solution of *p*TSA (ca. 1 mg mL^{-1}). The applied potential was increased in 25 mV steps: –0.50 V to +0.55 V vs Ag/AgCl. The inset photographs show the color states obtained upon electrochemical switching (neutral state on the left, fully oxidized state on the right).

films as a function of time at the polymer absorption maxima for potential steps ranging from 10 s to 0.25 s (**Figure 3a,b**). For the purpose of comparing the switching performance of PProDOT-acid versus that of PProDOT-ester, thin-films with nearly identical thickness (absorption maxima = 0.82 and 0.84 a.u., respectively) were spray-deposited and the best electrolyte salts found for each system were chosen to carry out this experiment. The square-wave potential steps were applied to PProDOT-ester in 0.2 M LiBTI/PC supporting electrolyte and to the water-processed PProDOT-acid in 1 M KNO_3/water supporting electrolyte. As illustrated in Figure 3b, the defunctionalized electrochrome PProDOT-acid switches with a contrast ratio (ΔT, where T is the optical transmittance of the film at a given wavelength) of ca. 60% at switching rates ranging from 10 to 0.5 s. In comparison, the pristine electrochrome PProDOT-ester processed from toluene performs similarly well at switching rates ranging from 10 to 0.5 s ($\Delta T \approx 65\%$), yet the loss of contrast on going from a rate of 0.5 to 0.25 s (≈13%) is considerably more pronounced than that seen with PProDOT-acid (≈3%). This result points toward faster ion diffusion processes for thin-films of the defunctionalized electrochrome PProDOT-acid, with the possibility that the presence of protic-polar carboxylic acid/carboxylate moieties impart the resulting films with a better affinity to the electrolyte. It is expected that the presence of apolar solubilizing side chains on the PProDOT-ester backbones hinders the diffusion of the doping ions across the thin film of electrochrome and impacts its response time at higher switching rates. Beyond the processing and film stability considerations, this constitutes a clear motivation for using defunctionalized electrochromes in ECDs with subsecond switching-time requirements.

A fresh film of PProDOT-acid was spray-cast from water onto ITO-coated glass and the long-term switching stability of the defunctionalized electrochrome was investigated at a switch time of 1 s per potential step in 0.2 M LiBTI/water supporting electrolyte. The polymer electrochrome demonstrated excellent redox stability, with less than 5% contrast variation over 16 000 cycles (square-wave potential steps of 1 s); this result strongly reinforces the potential of this technology for commercial applications. It is worth noting that, while slightly lower contrast ratios were produced when replacing KNO_3 by LiBTI, the latter proved to be a better electrolyte salt than KNO_3 for long-term switching stability experiments. This difference in long-term performance as a function of the electrolyte salt could be due to nucleophilicity or basicity effects in polar solvents such as water.

Using a simple homopolymer of dioxythiophene as an example, a π-conjugated polymer electrochrome bearing alkyl ester side-chains is chemically synthesized and subsequently defunctionalized to yield a polyionic salt with low aliphatic content that is readily soluble in water and further spray-processable from water. Upon neutralization, the defunctionalized polymer backbone recovers its electrochromic properties, switches faster than its substituted counterpart, and shows less than 5% of contrast variation over 16 000 switching cycles in water. Applied to polymer electrochromes, our side-chain defunctionalization approach adds the perspective for orthogonal depositions of multiple electrochromic "inks" to produce color states not readily achievable with a single polymer component. Beyond device engineering aspects, the ability to

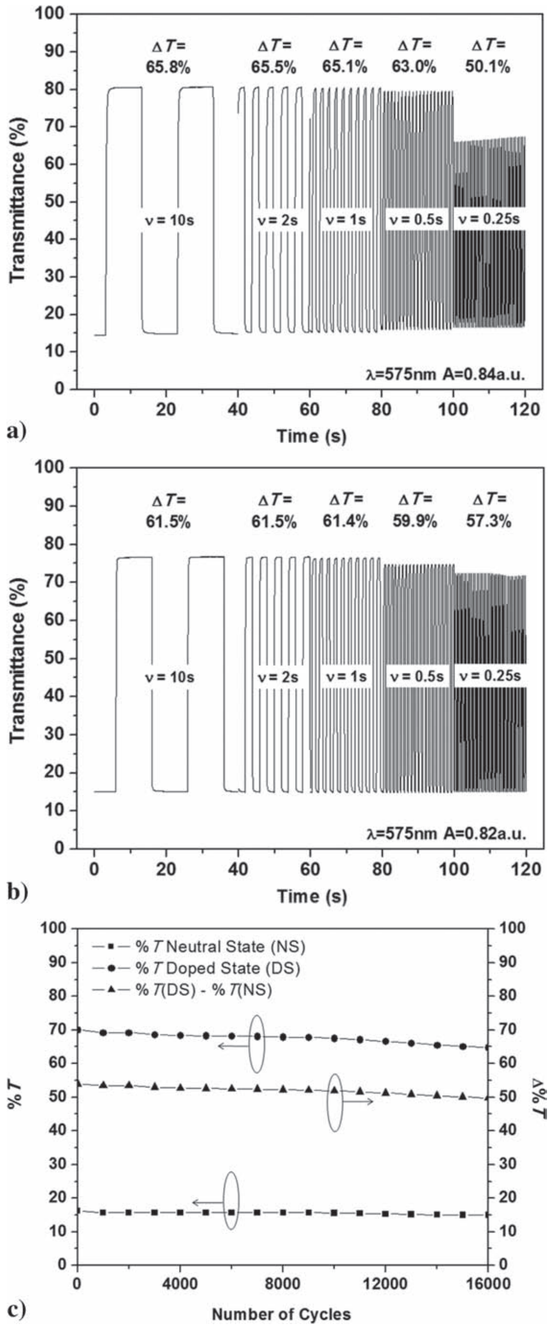

Figure 3. Polymer electrochromic performance. a) Square-wave potential step absorptometry of PProDOT-ester. The film was spray-cast onto ITO-coated glass from toluene and its transmittance was monitored at the polymer absorption maximum (575 nm) in 0.2 M LiBTI/PC solution. Switching potential range: –0.6 V to +0.475 V vs Fc/Fc^+. Switch times (ν): 10 s step for 40 s (2 cycles), 2 s step for 20 s (5 cycles), 1 s step for 20 s (10 cycles), then 0.5 s step for 20 s and 0.25 s step for 20 s from left to right. b) Square-wave potential step absorptometry of PProDOT-acid. The film was spray-cast onto ITO-coated glass from water and its transmittance was monitored at the polymer absorption maximum (575 nm) in 1 M KNO_3/water solution. Switching potential range: –0.65 V to +0.475 V vs Ag/AgCl. c) Long-term switching of PProDOT-acid on ITO in 0.2 M LiBTI/water solution (monitored at 575 nm), applying square-wave potential steps of 1 s (complete cycle is 2 s). Switching potential range: –0.65 V to +0.475 V vs Ag/AgCl.

print- or spray-process π-conjugated ECPs from aqueous media offers a sustainable alternative to using traditional organic solvent-processing methods and could rapidly impact the development of non-emissive flexible display technologies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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