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All-Printed Multilayers and Blends of Poly(dioxythiophene) Derivatives Patterned into Flexible Electrochromic Displays

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Low-cost, flexible and thin display technology is becoming an interesting field of research as it can accompany the wide range of sensors being developed. Here, the synthesis of poly(dimethylpropylene-dioxythiophene) (PProDOT-Me$_2$) by combining vapor phase polymerization and screen printing is presented. A multilayer architecture using poly(3,4-ethylenedioxythiophene) (PEDOT) and PProDOT-Me$_2$ to allow for electrochromic switching of PProDOT-Me$_2$, thereby eliminating the need for a supporting transparent conductive (metal oxide) layer is introduced. Furthermore, the technology is adapted to a blended architecture, which removes the additional processing steps and results in improved color contrast ($\Delta E^* > 25$). This blend architecture is extended to other conductive polymers, such as PEDOT and polypyrrole (PPy), to highlight the ability of the technique to adjust the color of all-printed electrochromic displays. As a result, a green color is obtained when combining the blue and yellow states of PEDOT and PPy, respectively. This technology has the potential to pave the way for all-printed multicolored electrochromic displays for further utilization in printed electronic systems in various Internet of Things applications.

1. Introduction

Electronic display technology is becoming a popular choice as informative indicators in low-power, low-cost Internet of Things (IoT) sensor systems. Various display technologies exist today, each with their advantages and disadvantages, but arguably the most promising technology when it comes to manufacturing cost, flexibility, thinness, and simple display architectures is printed electrochromic devices.[1]

Recent advances in materials, inks, and printing procedures have allowed for all-printed electrochromic displays in large volumes that currently are being incorporated in commercial markets.[2,3] Within these markets, arguably the most promising are electrochromic displays utilizing poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) due to their low-power consumption, printability, short switching time and good electrochromic contrast.[4,5]

Other conductive polymers require further development due to their insolubility, however, certain polymerization techniques have overcome this issue on the laboratory scale. Vapor phase polymerization (VPP) is one promising technique that has produced conductive polymers with excellent optical, electrical, and electrochromic properties.[6–9] The majority of reports within the scientific literature have utilized spin coating to produce thin films of the conductive polymers, which have then been incorporated into electrochromic devices.[10,11] While spin coating deposition possesses certain advantages for small-scale thin formation such as uniformity, it cannot be used when moving to large-scale manufacturing or when considering roll-to-roll production. Printing technologies are therefore more appealing when considering large area depositions. Several printing techniques have been combined with VPP, most of which have focused on achieving high-resolution patterns with very few showing large-scale production.[12] Screen printing is one printing technology that allows large-area deposition of functional inks into patterns with high resolution (≈70 µm). The alignment capability between layers also permits the overprintability of other inks, and thereby the formation of all-printed devices. Screen printing can also be adapted for either sheet-based printing or roll-to-roll manufacturing. Recently, we have shown that the VPP technique can be adapted for screen printing technology and that functional inks can be printed on the resultant conductive polymers for the fabrication of all-printed electrochromic devices, despite being based on insoluble conductive polymers such as polypyrrole (PPy) and polythiophene (PTh).[13]

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Within the recent report on combining VPP and screen printing, three conductive polymers, PEDOT, PPy, and PTh, were incorporated into all-printed, flexible electrochromic devices producing reflective displays that showed a light blue to dark blue, a grey to yellow, and a red to blue color change, respectively.[13] An alternative and interesting electrochromic conductive polymer is poly(dimethylpropylene-dioxythiophene) (PProDOT-Me_2).

Similar to PEDOT, PProDOT-Me_2 is a cathodically coloring polymer but possesses a higher color contrast without the undesired blue hue in the oxidized state, thus making it a great candidate as an active component of electrochromic displays. PProDOT-Me_2, with its impressive color contrast values, has previously been incorporated into electrochromic displays and even electrochromic sunglasses.[14,15] Moreover, its highly promising electrochromic properties in combination with its stability, allowed it to be used in reversible electrochromic mirrors, self-powered electrochromic displays, and in photovoltachromic applications.[16–19] However, similar to other conjugated polymers exhibiting low electronic conductivity, such as PPy and PTh, PProDOT-Me_2 requires a transparent conductive layer, usually indium tin oxide (ITO), in order to enable electrochromic switching. Researchers have provided alternatives to ITO to allow the electrochromism of PProDOT-Me_2. The group of Reynolds was one of the first to deposit a PEDOT:PSS layer, as a replacement of ITO, to create all-polymer electrochromic devices.[5] While successful, the device was a proof of concept and the printing of the materials was not included. Printing and patterning of PProDOT-Me_2 has been sparsely reported within the scientific literature. To the best of our knowledge, PProDOT-Me_2 has, due to its insoluble nature, either been modified to possess solubilizing side chains[20] or electropolymerized[21] on printed electrodes in order to pattern the conductive polymer. One report worth highlighting is the use of chemical vapor deposition and masking to achieve patterns of PProDOT-Me_2 on leaves for health monitoring.[22] However, chemical vapor deposition requires the vapors of both the oxidant and the monomer, and masking techniques limit the level of patterning possible.

Within this report, we report the first patterned films of PProDOT-Me_2 through the combination of vapor phase polymerization and screen printing. We have further optimized the oxidant screen printing ink for better printability in addition to better electrochromic properties, while we extended this technique to include the conducting polymer PProDOT-Me_2. Furthermore, we use a similar structure to the ones reported by Argun, et al.[5] by creating a VPP multilayer using PEDOT as the first layer to provide sufficient conductivity to enable electrochromic switching of the subsequently deposited PProDOT-Me_2, without the need of ITO, in flexible, thin, all-printed electrochromic displays. The concept of blends is then introduced to reduce the amount of processing steps while allowing better color contrast values. Finally, we show that these architectures can be used for other conductive polymers, such as PPy, to modify the color range of electrochromic displays and eventually achieve the fabrication of all-printed, organic, multicolor electrochromic displays.

2. Results and Discussion

Fabrication of multilayers and blend architectures has been reported previously and used to understand the growth of conductive polymers using the VPP method.[24] However, the previous report focused on their formation mechanisms; the structures were fabricated using spin coating and not incorporated in any practical devices. The multilayer and blend architectures and their fabrication are complex processes, therefore, **Figure 1** has been included to illustrate the different processing steps to create the different structures. Within Figure 1, both blends and multilayers are vertical, meaning the lower half is created with one conductive polymer and the top half is created with the second conductive polymer through a series of polymerization steps. The bottom-up mechanism of conductive polymer growth was studied in a previous report, which showed that the conductive polymer synthesized first will be located at the lower half of both blend and multilayer structures.[24] The main difference between the two structures is that the multilayer requires washing of the first conductive polymer being synthesized, followed by the deposition of a second oxidant layer, and finally the synthesis of the second conductive polymer. Whereas the blends are created using only one oxidant layer, and after the polymerization step in the first conductive polymer chamber the sample is immediately placed in the chamber of the second conductive polymer.

2.1. Oxidant Optimization

In order to achieve the goals, the oxidant ink was modified to improve printability. The previously reported oxidant ink was successful for the proof-of-concept organic electrochemical transistors and electrochromic devices, but only a minimal number of prints were possible before print fails occurred due to the ink possessing a "wax" like consistency.[13,23] To reduce the viscosity, but maintain the shear thinning, high resolution, and electrochemical properties, the amount of the triblock copolymer PEG-PPG-PEG was reduced and a random block copolymer PEG-ran-PPG was incorporated. The viscosities of both materials and the resultant oxidant ink compared to the previously reported oxidant ink can be found in the supporting information, see Figure S1, Supporting Information. Additionally, microscope images of the oxidant immediately after printing, after the heating step and after the polymerisation and washing steps are shown in Figure S2, Supporting Information. In Figure S2, Supporting Information, it can be seen that the high resolution of 100 µm lines and 100 µm spacing is maintained after the oxidant ink was modified.

In the process of creating a more suitable ink for screen printing and for multilayer and blend architectures, better performing all-printed electrochromic displays based on VPP-PEDOT:Otf and VPP:PPy:Otf were fabricated. The results can be seen in Figures S3, S4, and Table S1 in the supporting information, where the color contrast of the VPP-PEDOT:Otf samples increase from 21.0 to 27.3 with the newly developed oxidant ink.

The optimized screen printing ink was also suitable for the VPP of ProDOT-Me_2. High resolution (100 µm) structures can be seen in the supporting information (Figure S5) and all-printed electrochromic displays are shown in **Figure 2**. Figure 2A shows a photograph of two all-printed, flexible, reflective 7-segment electrochromic displays created using VPP-PProDOT-Me_2 as the electrochromic component. This type of display was selected to demonstrate that patterning of the dielectric layer in the stack allows an electrochromic pattern to be visible, similar to

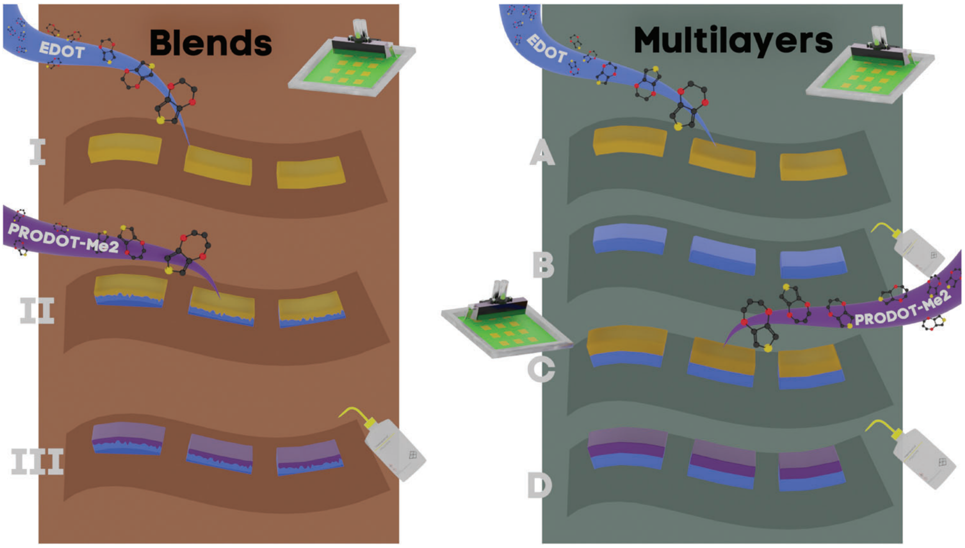
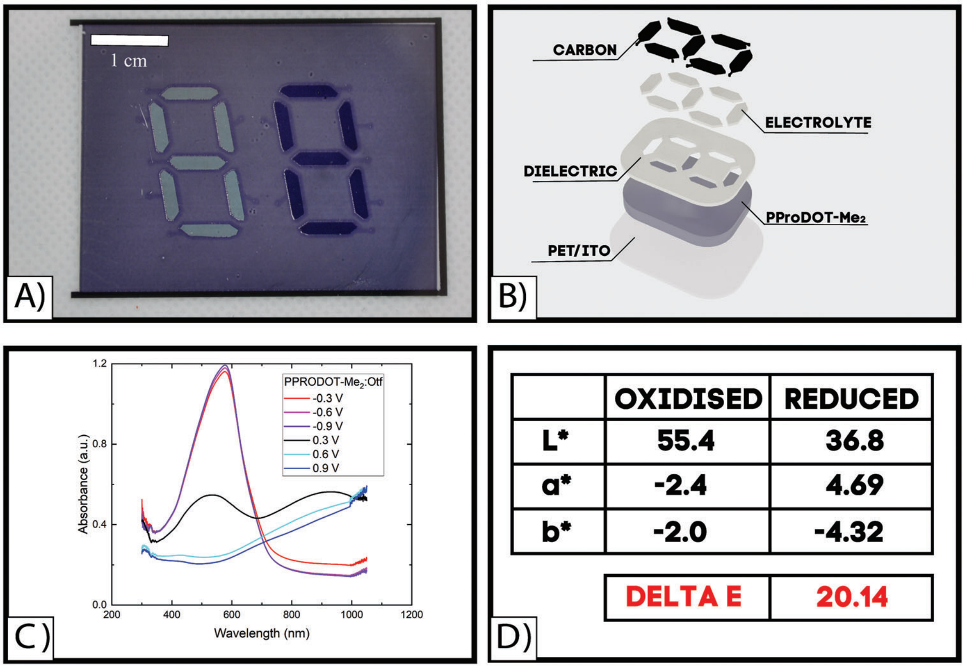


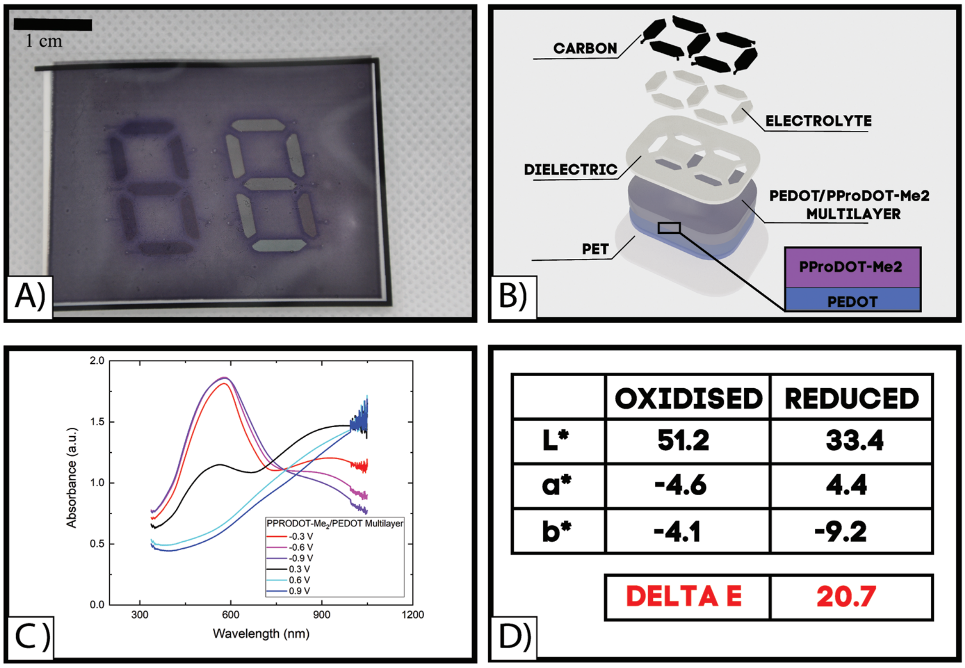
Figure 1. Graphical illustration of the manufacture of blends and multilayers. Blend manufacture: I) Screen printing deposition of an oxidant ink followed by EDOT exposure and II) subsequent exposure to ProDOT-Me_2 and III) rinsing with isopropanol resulting in a blend of the two conductive polymers. Multilayer manufacture: A) Screen printing deposition of an oxidant ink followed by exposure to EDOT, B) rinsing with isopropanol, C) screen printing deposition of another oxidant ink layer followed by exposure to ProDOT-Me_2 vapor and D) rinsing with isopropanol.



	OXIDISED	REDUCED
L*	55.4	36.8
a*	-2.4	4.69
b*	-2.0	-4.32
DELTA E	20.14	

Figure 2. A) All-printed electrochromic device incorporating VPP:PProDOT-Me_2 and ITO/PET as the substrate. B) Graphical illustration of an all-printed device. C) Spectroelectrochemical analysis and D) L^*, a^* b^* color coordinates of a square shaped display (1 cm^2 segment area) in its oxidized and reduced states and the corresponding ΔE^* color contrast value.

previous electrochromic displays developed by RISE.[25–27] Figure 2B illustrates the screen printed layers within the electrochromic device. Figure 2C shows the optical absorption spectra of only the PProDOT-Me_2 layer on an FTO substrate. The polymer switches to its purple dedoped state, with a strong absorption peak at 580 nm, already at voltages as low as –0.3 V, which is evidenced by the saturation of the electrochromic behavior for further elevated negative voltages, in comparison to other reported electrochromic conducting polymers where higher voltages are required in order for them to reach their fully dedoped state.[13] This electrochromic behavior of PProDOT-Me_2 highlights that display based on this system might require lower operating voltages. It is noted that there appears to be a total absence of any peak at ≈900 nm for the negative voltages, related to any



	OXIDISED	REDUCED
L*	51.2	33.4
a*	-4.6	4.4
b*	-4.1	-9.2

DELTA E	20.7

Figure 3. Multilayer architecture of VPP:PEDOT and VPP:PProDOT-Me$_2$ without ITO. A) All-printed flexible electrochromic display, B) Graphical schematic of the layer stack, C) Spectroelectrochemical analysis and D) *L**, *a** *b** color coordinates of a square shaped display (1 cm^2 segment area) in its oxidized and reduced states and the corresponding ΔE* color contrast value.

intermediate doping states.[28] Those states appear at 0.3 V and disappear into an IR shoulder, its transparent state at higher positive voltages. The appearance of the IR shoulder at higher positive voltages is in agreement with other reported conducting polymers. However, the appearance of two peaks at 0.3 V indicates that the conducting polymer is not fully doped yet and thus might lack in electrical conductivity, in comparison to the conventional PEDOT.[13]

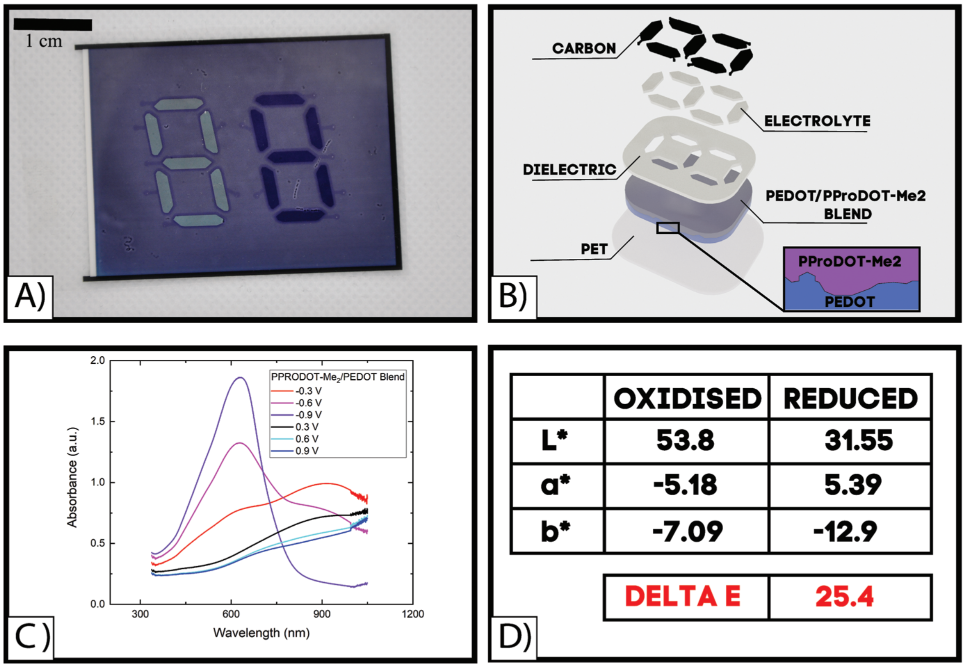
The $L^*a^*b^*$ color space of the device in its oxidized and reduced states is included in Figure 2D, showing good color contrast values of $\Delta E^* \approx 20$. This value, for a display not based on PEDOT:PSS, is considered good since other conductive polymers such as PPy-based all-printed displays have only reached a contrast value of $\Delta E^* \approx 17$.[13] Cyclic voltammetry of the PProDOT-Me$_2$ is shown in the supporting information (Figure S6).

However, the above all-printed electrochromic device is printed on ITO-coated PET since electrochromic switching is prevented due to the low conductivity of the PProDOT-Me$_2$ film itself (see Figure S7, Supporting Information). Besides the additional cost of using ITO-coated substrates, they are also unsuitable for electrochemical stability reasons within this system. Employing printed carbon counter electrodes within the printed electrochromic displays requires high voltages to achieve good switchability. Unfortunately, these voltages are above the operation voltage of ITO. Additionally, global conductive (ITO) layers make silver connecting lines impossible due to electronic short circuits occurring and patterning of ITO for each display design is problematic. Therefore, it was hypothesized that a multilayer architecture, where a thin layer of PEDOT is synthesized followed by a thicker layer of PProDOT-Me$_2$, would allow a PET substrate to be utilized without the ITO coating.

2.2. Multilayer Architecture

The multilayer structures were fabricated from a sequential VPP process using screen printing (aligned) for the oxidant deposition. This process allows subsequent layers to be screen printed on top of the conductive polymers to create a functional, all-printed electrochromic display. The concept behind this architecture is that the PEDOT will act as the conductor while being thin enough to not contribute to the color change in the electrochromic switch (or to a very limited amount). A flexible, all-printed, multilayer electrochromic display of PEDOT and PProDOT-Me$_2$ is shown in **Figure 3**. A separate device showing the individual layers of the multilayer more clearly can be seen in the supporting information (Figure S8). A photograph of the 7-segment display in its reduced (left) and oxidized (right) states is presented in Figure 3A, while the order of the screen printed layers can be viewed in Figure 3B. The inset within Figure 3B illustrates the sharp interface between the two conductive polymers due to the layers being deposited by using separate oxidant prints. Figure 3C shows the spectra of only the multilayer structure on an FTO substrate and is similar to the individual PProDOT-Me$_2$ spectra with some PEDOT contributions, which were to be expected. Indeed, the multilayer system exhibits a wider absorption peak at ≈580 nm, which also saturates at −0.3 V, similar to Figure 2C of the pure PProDOT-Me$_2$ system, but it also exhibits the highly doped and conducting aspects of PEDOT, which are reflected both in the gradual decrease of the intermediate states at ≈900 nm at negative voltages and in the sharper IR shoulder at positive voltages.

The $L^*a^*b^*$ color space of the device in its oxidized and reduced states is also included in Figure 3D, which maintains the



	OXIDISED	REDUCED
L*	53.8	31.55
a*	-5.18	5.39
b*	-7.09	-12.9

DELTA E	25.4

Figure 4. Blend architecture of VPP:PEDOT and VPP:PProDOT-Me_2 without ITO. A) Photograph of an all-printed flexible electrochromic display, B) Graphical schematic of the layer stack, C) Spectroelectrochemical analysis and D) L^*, a^* b^* color coordinates of a square shaped display (1 cm^2 segment area) in its oxidized and reduced states and the corresponding ΔE^* color contrast value.

good color contrast shown in the single layer of PProDOT-Me_2. Cyclic voltammetry of the PEDOT/PProDOT-Me_2 multilayer on FTO is shown in the supporting information (Figure S9).

The appearance of the multilayers is poor when compared to the sharpness of the PProDOT-Me_2 on ITO in Figure 2. Additionally, these multilayer structures are more complex to fabricate due to the need of a second layer of oxidant ink followed by additional VPP and washing steps. Regarding processability and commercialization, the addition of extra steps in the process is undesirable. The multilayers are also prone to become darker due to the difficulty in producing thin layers. This results in a lower color contrast value. These issues mentioned above can be solved by switching to a blended architecture.

2.3. Blend Architecture

Due to the nature of the VPP process, i.e., the introduction of monomer vapor into a chamber and polymerization on a liquid oxidant, the opportunity to synthesize two conductive polymers with a single oxidant layer is possible, thereby creating a conductive polymer blend. Since only one oxidant layer is used in the blend formation, the resulting film can be thinner and therefore more transparent, which generally results in better color contrast values. However, if thicker layers are required, the ink can be modified to achieve this. It is expected that the interface between the two conductive polymers in the blend architecture is "blurred", which may be more beneficial for the electrical properties (through less interfacial resistance) and aids the adhesion of the second conductive polymer layer. This architecture has been previously reported, although not in printed and patterned form.[24] The removal of one washing step and the second oxidant print of the blend architecture creates a different interface between the two conductive polymers as compared to the multilayers, in which interfacial mixing between the two conductive polymers is prohibited.

A flexible, all-printed electrochromic display based on the blend of PEDOT and PProDOT-Me_2 is shown in **Figure 4**. A photograph of the 7-segment display in its oxidized (left) and reduced (right) states is presented in Figure 4A, while the order of the screen printed layers can be viewed in the graphical schematic in Figure 4B. The inset within Figure 4B illustrates the blended interface between the two conductive polymers due to the layers being synthesized with the same oxidant print. Figure 4C shows the spectra of only the PEDOT/PProDOT-Me_2 blend structure on an FTO substrate and is similar to the individual PProDOT-Me_2 spectra with some PEDOT contributions, which again were to be expected. In comparison to Figure 3C, the spectra of Figure 4C show more of a combined behavior between PProDOT-Me_2 (Figure 2C) and PEDOT. In the same manner, as PEDOT films, the polymer blend film is gradually dedoped until reaching its fully dedoped state at −0.9 V. The polymer blend film, in a similar behavior as PProDOT-Me_2, exhibits a sharper peak than a film of only PEDOT. However, the contribution of the included PEDOT shifts the peak from 580 nm to 630 nm. Additionally, the blends appear to be more transparent at lower positive voltages in comparison to the individual PProDOT-Me_2 film, which is related to the highly conducting nature of PEDOT.[13]

The $L^*a^*b^*$ color space of the device in its oxidized and reduced states is also included in Figure 4D, which shows improved color contrast even compared to the individual PProDOT-Me_2. This color contrast value of $\Delta E^* \approx 25$ is comparable to

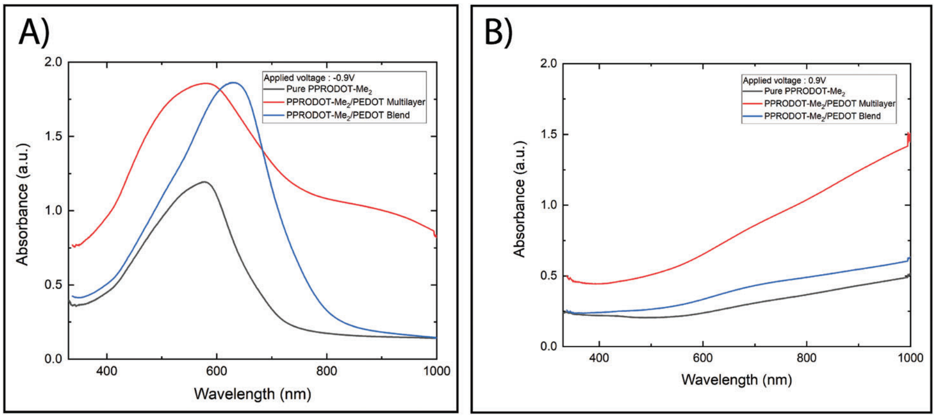


Figure 5. Spectral comparison between an individual PProDOT-Me$_2$ film, a multilayer, and a blend of PEDOT and PProDOT-Me$_2$. An applied voltage of A) −0.9 V and B) +0.9 V is used.

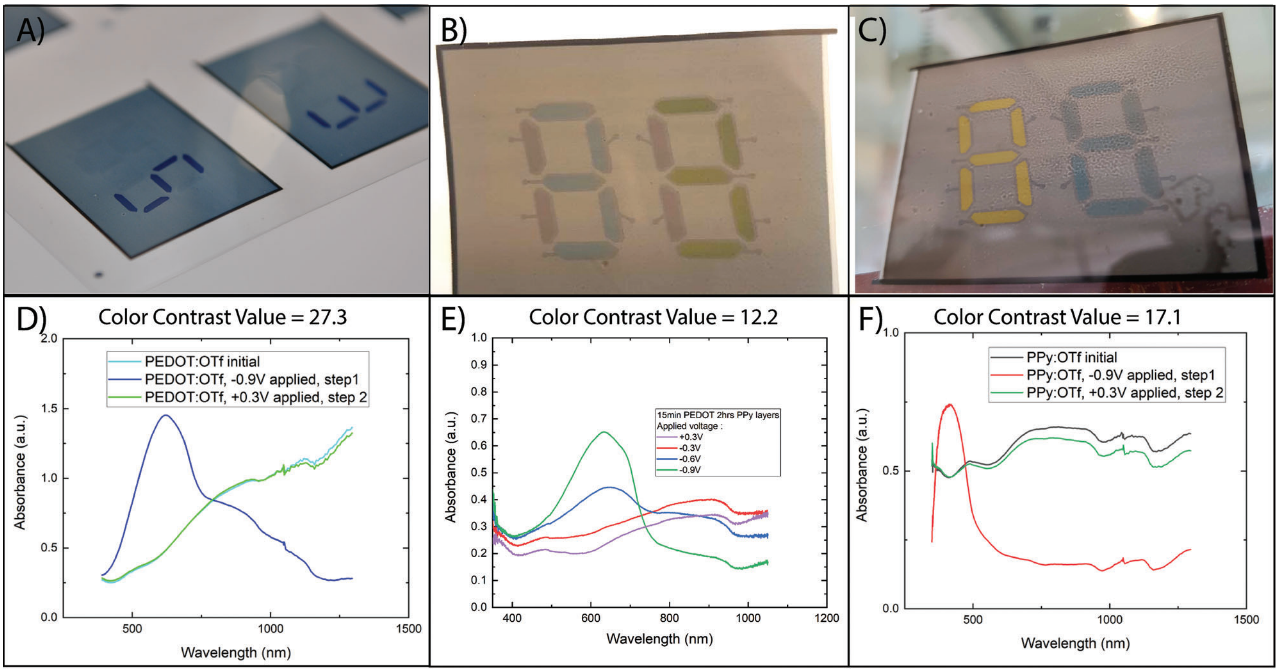


Figure 6. Comparisons between individual PEDOT, individual PPy, and a blend of the two showing a combination of their colors, the films are produced by screen printing the oxidant layer followed by VPP. Photographs of all-printed electrochromic displays of A) PEDOT, B) PEDOT/PPy blend and C) PPy. Optical absorption spectra of D) PEDOT, E) PEDOT/PPy blend and F) PPy deposited on FTO-coated glass.

PEDOT:PSS-based devices used in commercial display products, thereby showing the great potential of this technology. Cyclic voltammetry of the PEDOT/PProDOT-Me$_2$ blend on FTO is shown in the supporting information (Figure S10).

As a complement to the previous comparative discussion on the spectra of the different architectures, **Figure 5** presents a direct comparison of the spectra between the individual PProDOT-Me$_2$, the PEDOT/PProDOT-Me$_2$ multilayer, and the blend architectures. Within Figure 5, the obvious shift in wavelength peak for the blend architecture can be observed in comparison to the multilayer and individual PProDOT-Me$_2$. The exact nature of this shift is currently unknown, but the absorption spectra of the blend films may suggest that the PEDOT and PProDOT-Me$_2$ in the blend architecture are forming copolymers rather than a blend of the two homopolymers. However, there seems to be confusion within the scientific community as to which is formed when two conductive polymers are synthesized at similar times, with both copolymers and blends being previously reported during simultaneous VPP.[29,30] Further experimental work outside of the scope of this study is required for a definitive answer on this hypothesis. Additionally, the absence of a peak at ≈900 nm and the higher sharpness of the peak of the blend architecture can explain its higher color contrast in comparison to the multilayer architecture.

As mentioned in the previous section, these architectures can be applied to other conductive polymers. The goal of the activities

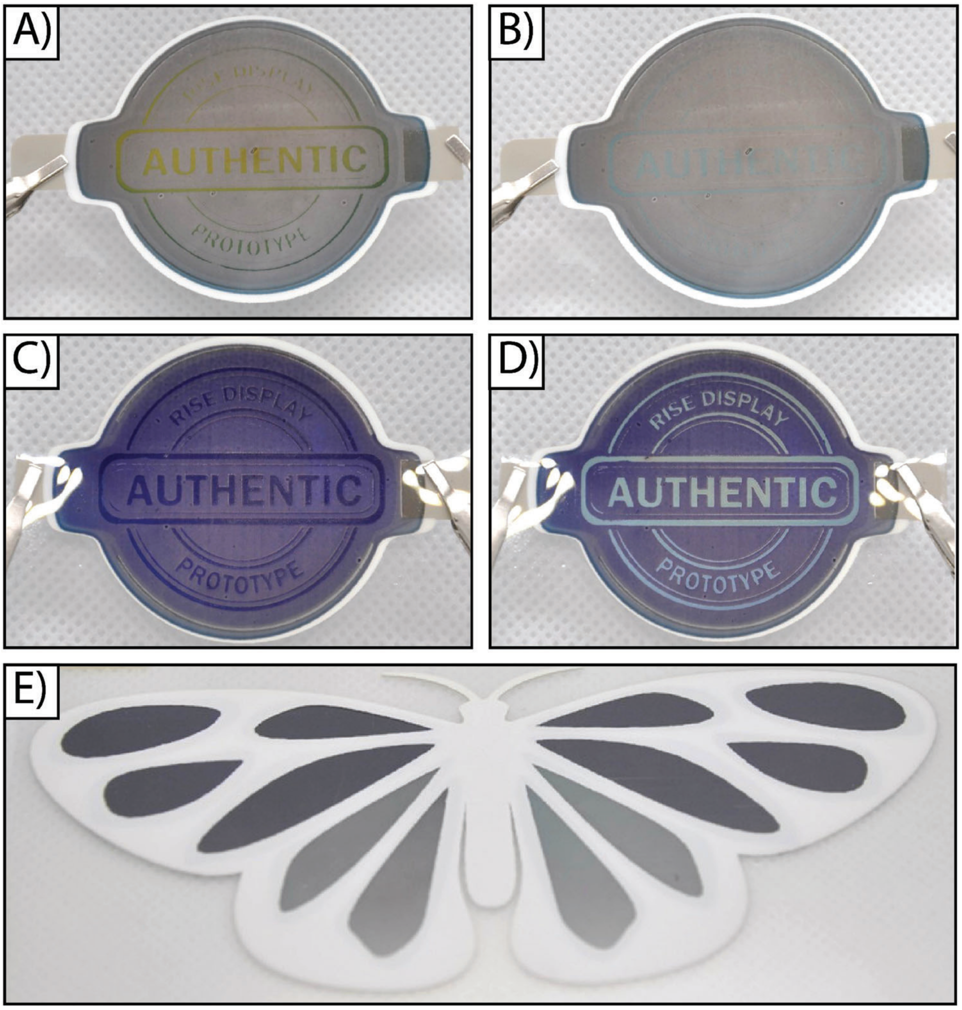


Figure 7. All-printed electrochromic displays in various designs highlight the potential of these multicolored materials. PEDOT/PPy blends in an authentic label design showing the A) reduced and B) oxidized states. PEDOT/PProDOT-Me_2 blends in an authentic label design showing the C) reduced and D) oxidized states, and E) a butterfly design using the PEDOT/PProDOT-Me_2 blend with the top half section being reduced and the lower half being oxidized.

described above was to allow an all-printed electrochromic device incorporating VPP:PProDOT-Me_2 without the need of ITO. However, these architectures can also be utilized in order to modify the colors of the resultant conductive polymer layers. To highlight this idea, blend architectures of PEDOT and PPy were created. The combination of PPy and PEDOT allows a green color to be displayed as the PEDOT is darkened to a blue state when the PPy concurrently is lightened to a yellow state. This complementary electrochromic behavior has a negative effect on the color contrast value but permits a multicolor all-printed electrochromic display, as shown in **Figure 6**. Pristine PEDOT (Figure 6A,D) and pristine PPy (Figure 6C,F) are compared to a blend of the two conductive polymers (Figure 6B,E). The photographs show that a mix of the two polymers has been produced with the characteristic yellow-colored state of reduced PPy being modified to a green color.

The characteristic peak in the reduced state of PPy at ≈400 nm is missing in the spectra of the blend shown in Figure 6E, but it may have been shifted to longer wavelengths and merged with the characteristic peak of reduced PEDOT. This is observed in three different samples of the blends (each one with a different polymerization time) and shown in the supporting information (Figure S11). The corresponding $L^*a^*b^*$ colors of the devices when switched to different oxidation states are shown in Figure S12, Supporting Information.

Finally, we present all-printed electrochromic displays incorporating blends of PEDOT/PPy and PEDOT/PProDOT-Me_2 in more interesting patterns than the square shaped display segments and the seven-segment displays described in previous tests, to further demonstrate the versatility of the printing technology, see **Figure 7**.

3. Conclusions

To conclude, we have optimized the oxidant ink for the combination of vapor phase polymerization and screen printing, which has improved both the properties of the conductive polymers, such as PEDOT and PPy, and the performance of the electrochromic displays that were fabricated with this method. The combination of technologies was extended to include PProDOT-Me_2, and its incorporation into all-printed electrochromic devices is also presented. In order to replace the ITO layer we produced a multilayer architecture of PEDOT and PProDOT-Me_2, which permitted electrochromic switching of PProDOT-Me_2 due to only a minimal polymerization time of EDOT. To avoid additional processing steps, we also introduced the conductive polymer blend concept, which has two conductive polymers synthesized by just using one printed oxidant layer. The blends of PEDOT and PProDOT-Me_2 resulted in flawless all-printed electrochromic displays that possessed the best contrast values, again without the requirement of an ITO layer. The concept of conductive polymer blends was then extended to show a modification of colors using PEDOT and PPy blends to create also a green-colored state. As a proof of concept, these methods were then incorporated in flexible, all-printed, multicolor electrochromic displays to highlight the potential of the technology in future electronic systems requiring simple low-cost indicators within the application domain of the Internet of Things.

4. Experimental Section

Materials: 3,4-(2,2-Dimethylpropylenedioxy)thiophene was purchased from Sycon Polymers India Pvt. Ltd. Purification was performed by making a milky white dispersion of the monomer in hot water by sonication. The milky white liquid was collected, and the monomer was extracted using hexane.

Pyrrole, 3,4-ethylenedioxythiophene and poly(ethylene)glycol-poly-(propylene)glycol-poly(ethylene)glycol (PEG-PPG-PEG) (5800 g mol^{-1}), poly(ethylene)glycol-ran-poly(propylene)glycol (PEG-ran-PPG) (12000 g mol^{-1}) and Phosphate Buffer Saline tablets were purchased from Sigma Merck. Iron (III) trifluoromethanesulfonate (FeOtf)was purchased from Pure Chemistry Scientific Inc.

The silver (5000) and carbon (7102) inks were purchased from DuPont, the dielectric (UVAR) was purchased from Marabu, the PEDOT:PSS (S V4) ink was purchased from Heraeus, the electrolyte (E003) ink was provided by RISE. The functional inks were deposited by screen printing on PET substrates (Polifoil) purchased from Policrom.

ITO-coated ($\approx$50 $\Omega\ \square^{-1}$) PET substrates were purchased from Eastman. FTO-coated glass substrates were purchased from Redoxme.

Methods: Combining screen printing and vapor phase polymerized conductive polymers was achieved similarly to previous reports.[13,23] However, the oxidant ink was modified to improve printability.

Fe(Otf) (9 wt.%) was mixed in water and followed by the addition and melting of PEG-PPG-PEG (15.2 wt.%) and PEG-ran-PPG (30.3 wt.%) on a 100 °C hotplate. Once melted (with the aid of a magnetic stirrer bar) the ink was mixed in a DAC 600.1 – CM 50 SpeedMixer at 2000 rpms for 8 min.

Fabrication of the individual conductive polymers (PProDOT-Me_2, PEDOT, PPy) was achieved by using a semi-automatic EKRA screen printer to deposit the oxidant ink in a pattern designed for electrochromic devices (and to obtain high resolution). The screen meshes were 120–34 (120 fibers per cm with a fiber diameter of 34 µm). The oxidant ink was deposited onto various substrates (PET, ITO-coated PET, and FTO-coated glass) and then heated on a 100 °C hotplate for 30 s to allow the imprinted screen mesh to spread and become a uniform coating before being placed in the VPP chamber.

Separate VPP chambers were used for the different conductive polymers to avoid contamination. The chambers were composed of sealed boxes that could accommodate an A4 sheet with space for a small reservoir of monomer (excess for the polymerization). The polymerization time for the PPy was 2 h, while the PEDOT polymerization time was 3 h to achieve even coatings. The PProDOT-Me_2 synthesis was performed on a hotplate at 100 °C for 1 h. After the polymerization, the samples were placed on a 70 °C hotplate for 2 min to complete the polymerization, followed by a washing step with isopropanol (IPA) and air dried with compressed air.

Multilayer structures of the conductive polymers were fabricated by screen printing the oxidant ink followed by heating the samples on a 100 °C hotplate for 30 s. The samples were then placed in the EDOT VPP chamber for 10 min, unless otherwise stated, before being placed back on the 100 °C hotplate for 2 min to allow completion of the polymerization. The samples were washed in IPA and air dried before a second oxidant ink layer was aligned and deposited by screen printing. The PEDOT layer and the newly deposited oxidant were heated on a 100 °C hotplate for 30 s before being placed in the PProDOT-Me_2 or pyrrole VPP chamber for 1 h and 2 h, respectively, and then back on the 100 °C hotplate for 2 min. The multilayered samples were washed in IPA and air dried, to prepare them for further analysis or subsequent screen printing into functional devices.

Conductive polymer blends were achieved by screen printing the oxidant ink followed by heating the samples on a 100 °C hotplate for 30 s. The samples were then placed in the EDOT VPP chamber for 10 min, unless otherwise stated, before being placed back on the hotplate for another 30 s. The samples were then placed into the ProDOT-Me_2 or pyrrole VPP chambers for 1 h and 2 h, respectively, and then back on the 100 °C hotplate for 2 min. The blends were washed in IPA and air dried, to prepare the samples for further analysis or subsequent screen printing into functional devices.

Rheological profiles were recorded with an MCR 102 rheometer from Anton Paar. A cone and plate geometry (D: 50 mm, 1 °) with a gap distance of 0.102 mm was used for all the measurements (environmental condition: temperature 21 ± 1 °C and relative humidity (RH) of ≈45%–50%). The samples were pre-sheared (1 s^{-1} for 60 s) before viscosity profiles were produced.

Characterization of Patterned Thin Films: Spectroelectrochemical measurements were recorded by a AvaSpec Fiber Optic absorption spectrometer, while the samples were connected with a Biologic Potentiostat SP-200. For both the spectroelectrochemical experiments and the cyclovoltammetry experiments a Pt-wire counter electrode and an Ag/AgCl reference electrode were used. A PBS tablet was dissolved in H_2O yielding 0.01 M of phosphate buffer, which was used as the electrolyte in both spectroelectrochemical and cyclovoltammetric experiments.

Color contrast values were recorded by a Mercury spectrophotometer from Datacolor using a white tile and light trap as calibration. The color coordinates, expressed as CIE $L^*a^*b^*$ values, were obtained and the color contrast (ΔE^*) was calculated using Equation (1):

$$\Delta E^* = \sqrt{\left(L_2^* - L_1^*\right)^2 \left(a_2^* - a_1^*\right)^2 + \left(b_2^* - b_1^*\right)^2} \qquad (1)$$

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

electrochromic displays, PEDOT, PProDOT-Me_2, screen printing, vapor phase polymerization

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