

A vapor printed electron-accepting conjugated polymer for textile optoelectronics

David Bilger, Kwang-Won Park, Trisha L. Andrew*

Department of Chemistry, University of Massachusetts, Amherst, MA 01003, United States

ARTICLE INFO

Keywords:

Vapor printing
Cyclopentadienone
Acceptor

ABSTRACT

Reactive vapor printing has emerged as an advantageous method to create conjugated polymer films with enviable electronic properties on prewoven fabrics. However, the conjugated polymers that have been vapor printed to date are exclusively hole transporters, since only monomers that can form radical cations participate in the oxidative polymerization reaction that underpins all existing vapor printing recipes. Here, we vapor print a conjugated polymer, **PDTCPD**, containing electron-withdrawing cyclopentadienone (CPD) moieties that depress its electronic energy levels and qualify it to serve as an electron acceptor when interfaced with known vapor-printed polymers. A custom-built hot wall reactor is shown to enable vapor-phase oxidative polymerization of a heavy CPD derivative to create **PDTCPD** films. Vapor printing is particularly useful for creating films of CPD-containing polymers because these intractable materials cannot be processed using solution-based methods. Vapor printing yields uniform and conformal **PDTCPD** films on topographically complex fabrics with minimal evident erosion upon solvent rinsing. This work provides a route to construct wearable optoelectronic devices that include monolithically-integrated active layers.

1. Introduction

Reactive vapor printing has emerged as an advantageous method to create conjugated polymer films with enviable electronic properties on densely-textured, patterned, and/or flexible substrates [1–4]. Vapor printing is particularly useful for making electronic textiles, where reliably coating electronic materials onto disordered yarned threads or prewoven fabrics remains a challenge [5].

While variations in reactor geometry and deposition algorithms for vapor printing conjugated polymers have been explored [1–4], an oxidative polymerization is the sole chemical reaction that underpins all existing techniques [6]. In this reaction, an electron-rich, typically-heterocyclic monomer is chemically oxidized to form reactive radical cations that dimerize and, subsequently, chain extend (obeying step-growth kinetics). Inside the reactors used to vapor print polymers, monomer oxidation and dimerization occur in the vapor phase, whereas chain extension primarily occurs on a substrate surface [7]. This surface-restricted growth process leads to remarkably conformal coatings on diverse substrates.

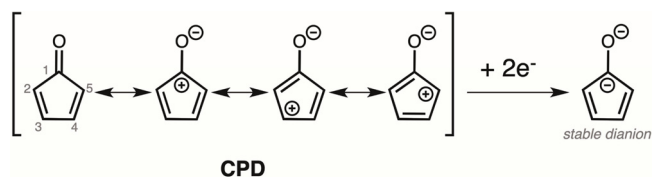
Due to the constraints of the oxidative polymerization reaction (i.e., only monomers that can form radical cations are applicable), the conjugated polymers that have been vapor printed to date are exclusively hole transporters [1,6]. Such limited scope in accessible polymers curbs

development of vapor-printed diodes for optoelectronic devices, which require both hole and electron transporting polymers to construct Type-II heterojunctions [8]. Feasible recipes for vapor printing electron-accepting and/or electron-transporting polymers would enable construction of a number of unique wearable devices, such as monolithically-integrated fabric solar cells and fiber-based light emitting diodes that retain the comfort, hand-feel, and breathability of familiar textiles.

Here, we vapor printed a conjugated polymer, **PDTCPD**, with especially low-lying band energies, which can serve as an electron acceptor when interfaced with known vapor-printed polymers. Low-lying band edges were achieved by incorporating an electron-withdrawing cyclopentadienone (CPD) moiety into the repeat unit of the conjugated polymer (Scheme 1). Cyclopentadienones are attractive “acceptor” units that reduce the barrier for electron injection into a conjugated system and afford *n*-dopable conjugated polymers with notable electron mobilities [9–11]. Although Wudl et. al previously synthesized a small library of low band-gap monomers and polymers containing CPD moieties [9–11], these polymers could not be readily solution processed and, therefore, did not find wide use in contemporary devices. We recognized, however, that the high thermal stabilities of 2,5-aryl-substituted CPD derivatives render them ideal precursors for reactive vapor printing, which is not governed by solubility concerns.

* Corresponding author.

E-mail address: tandrew@umass.edu (T.L. Andrew).



Scheme 1. The cyclopentadienone (CPD) acceptor moiety.

2. Results and discussion

We identified a CPD derivative, **DTCPD**, as a pilot precursor for this study and synthesized it following a previously-reported procedure. [12] The purity of the synthesized monomer was confirmed via ^1H and ^{13}C NMR spectroscopy. **DTCPD** contains electron-rich thiophene substituents in the 2,5-positions of the CPD ring, which are twisted out of conjugation with the CPD ring and, consequently, can be oxidized by iron(III) chloride despite the presence of an electron-withdrawing moiety; indeed, Wudl et al. previously reported the solution-phase oxidative polymerization of a similar analog. [9] **DTCPD** is an uncharacteristically heavy monomer (MW = 396.52 g/mol), as compared

to typical precursors for vapor printed polymers (MW < 150 g/mol) [6]. For this reason, we used a custom-built tubular hot-wall reactor (Fig. 1a) with short linear path lengths to effect vapor-phase oxidative polymerization. [3] **DTCPD** and FeCl_3 powders were loaded into crucibles and placed, along with target substrates, in a linear geometry inside the reactor. The placement order depicted in Fig. 1a, with substrates placed between the two crucibles, was empirically determined to afford the most uniform and reproducible coatings across multiple deposition batches.

Upon separately heating the monomer and oxidant crucibles, vapors of each component travelled horizontally and intersected over a finite region where an insoluble black coating evolved, which we tentatively assigned as **PDTCPD**. The spatial extent of the intersection region (visualized by the black coating) could be controlled by changing a combination of the monomer and oxidant heating temperatures and tuning the base pressure of the reactor using a low flow (< 2 sccm) of nitrogen gas. Substrates placed in the intersection region were uniformly coated with an insoluble black film (Figure S1) and the coating thickness could be controlled by varying the deposition time (the average growth rate was 0.5 nm per minute). Substrates were rinsed after deposition to remove residual metal salts and other reaction

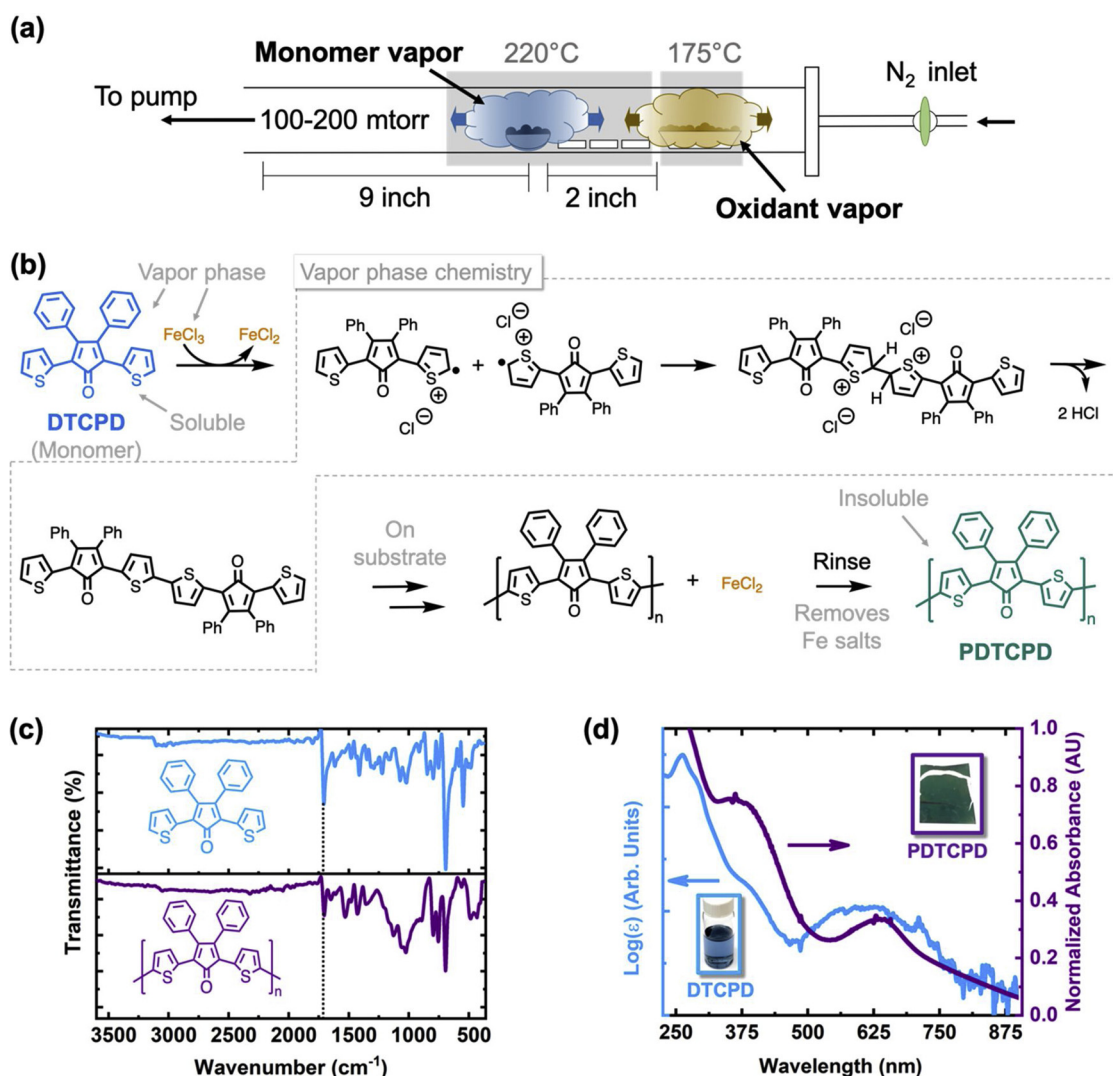


Fig. 1. (a) Schematic of the reactor used to vapor print conjugated polymers starting from heavy monomers. (b) Proposed reaction mechanism for oxidative polymerization of monomer **DTCPD** with an iron(III) chloride oxidant inside our reactor to afford vapor printed **PDTCPD** films. (c) IR spectra of the monomer **DTCPD** and the vapor printed polymer isolated from the reactor. (d) UV-vis absorption spectra of the monomer **DTCPD** (dichloromethane solution, blue line) and the vapor printed polymer film on glass (purple line). The insets are optical images of these two samples (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

byproducts (Figure S2), leaving behind a dark green-black film.

Fig. 1b illustrates the proposed reaction mechanism for forming PDTCPD in our reactor. The IR spectrum of a vapor-printed film resembled that of the monomer DTCPD (powder), including a strong carbonyl stretching band at 1707 cm^{-1} (Fig. 1c). The notable complexity observed in both IR spectra likely resulted from the numerous stretching and rotational modes available to the repeat unit structure. Further, the UV-vis absorption spectrum of the vapor printed film revealed two major bands, centered at 360 nm and 640 nm (Fig. 1d), which we assigned to the characteristic $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions of the CPD moiety, respectively. Similar optical transitions were also evident in the monomer, suggesting that the important CPD moiety was preserved in the vapor-printed PDTCPD films. Further, minimal bathochromic shifting between the absorption bands of the monomer and the vapor printed film were observed, precluding the possibility of intramolecular cyclization side reactions during polymerization.

The valence band spectrum and the corresponding secondary electron cutoff photoemission spectrum of three approximately 100 nm thick films of PDTCPD on ITO were measured using ultraviolet photoelectron spectroscopy (UPS). A valence band spectrum reveals the condensed-phase binding energies (vs. vacuum level) of all the occupied electronic states of the polymer. Vapor-printed PDTCPD possessed an especially deep valence band edge averaged at $-6.7 \pm 0.2\text{ eV}$

(Fig. 2a). Such a low-lying valence band edge was expected. First, the electron-withdrawing CPD moiety should depress the band energy levels of a π -conjugated system [9,11]. Second, the presence of two bulky phenyl substituents in the repeat unit of PDTCPD should inhibit backbone planarization and interchain stacking, further limiting the effective conjugation length of the polymer [13]. This effect is supported by the previously discussed UV-vis measurements, which demonstrate minimal (ca. 15 nm) bathochromic shifting between the absorbance bands of PDTCPD and those of its monomer (Fig. 1d). The optical band gap of PDTCPD was calculated to be 1.5 eV, based on the absorption onset of the lowest-energy $n\text{-}\pi^*$ band.

Fig. 2b compares the band edge energies of vapor printed PDTCPD with notable hole and electron transporting materials. Importantly, previously-reported vapor-printed polymers (polythiophene [14] and polyisothianaphthene [15]) show band edges similar to prevalent hole transporters, including P3HT, [16] DBP [17], and PTB7 [18]. In contrast, the band energy levels of vapor-printed PDTCPD are closer to those of canonical electron transporting materials, such as ICBA, [19] PCBM [18], and C₆₀ [20]. Therefore, vapor-printed PDTCPD should act as an electron-accepting material when interfaced with other known vapor printed polymers.

The primary advantage of reactive vapor printing is its ability to conformally coat non-planar, patterned or textured surfaces with

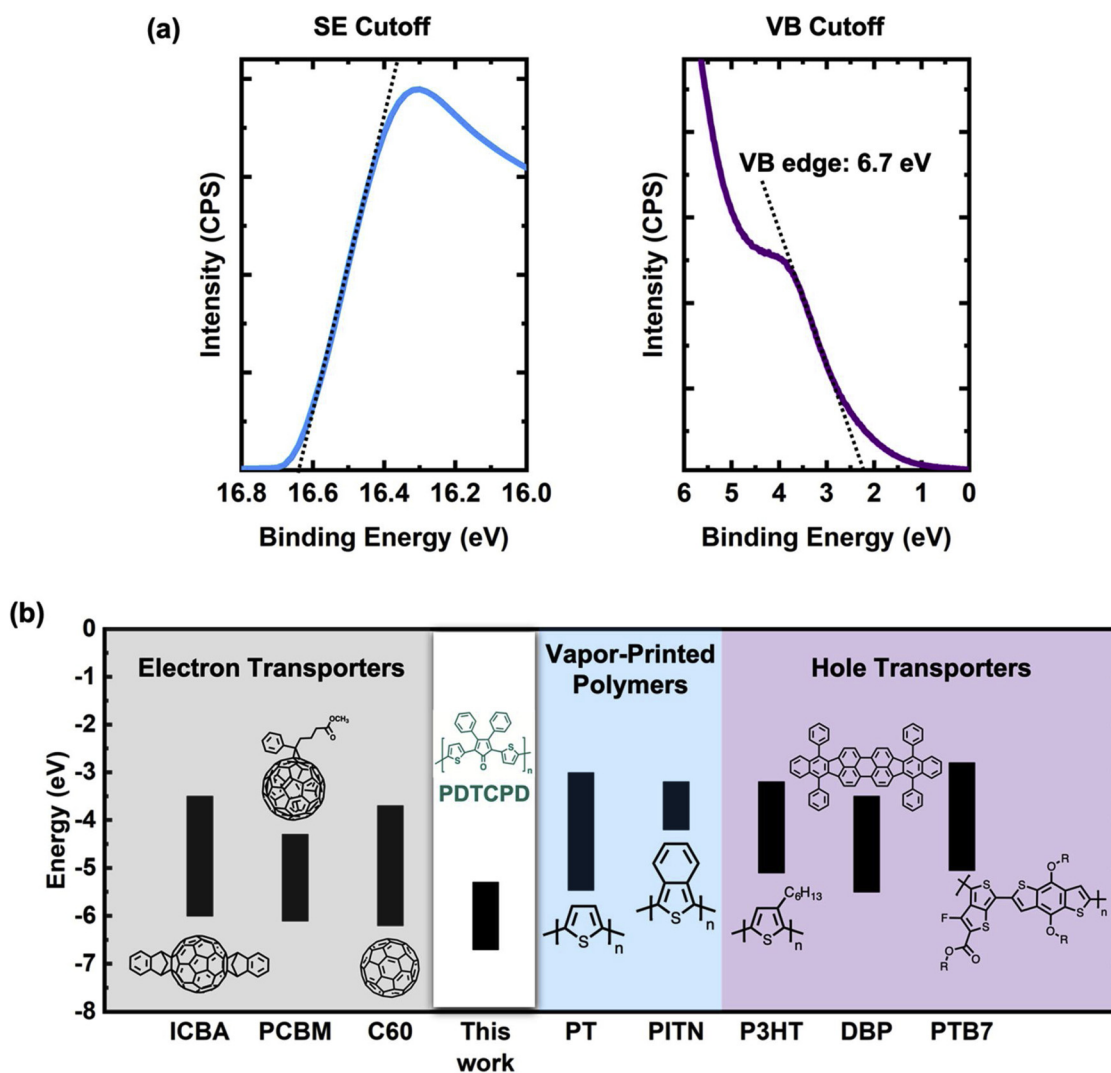


Fig. 2. (a) Representative secondary electron cutoff photoemission spectrum (left) and the corresponding valence band spectrum (right) of vapor-printed PDTCPD on ITO. (b) Comparison of the band edge energies of PDTCPD with notable hole and electron transporting materials. The valence band edge of PDTCPD (given above) was directly measured as an average of three samples via ultraviolet photoelectron spectroscopy and its conduction band edge was calculated from the optical gap.

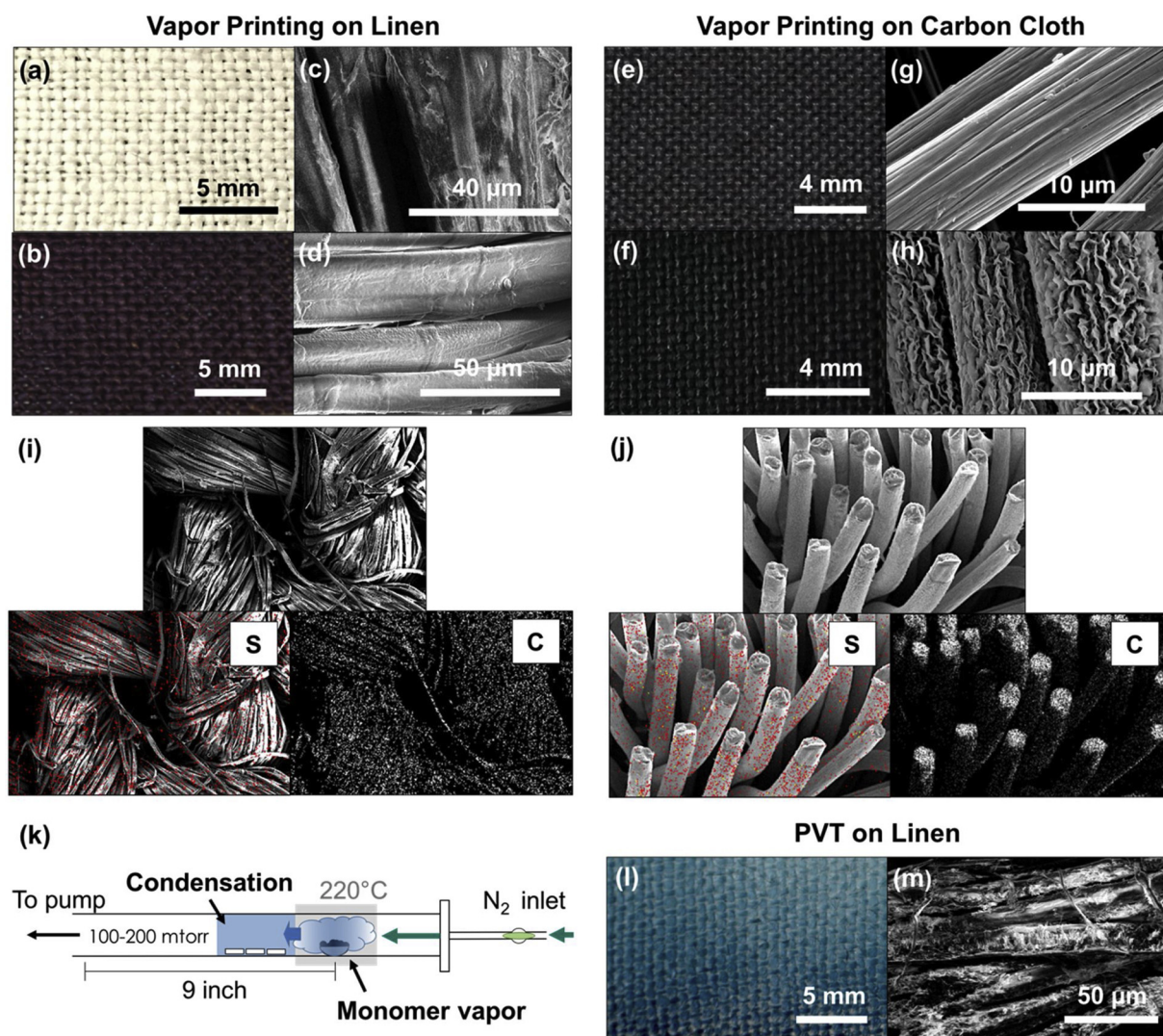


Fig. 3. Optical images of (a) pristine and (b) PDTCPD coated linen. Scanning electron micrographs (SEMs) of (c) pristine and (d) PDTCPD coated linen. Optical images of (e) pristine and (f) PDTCPD coated carbon cloth. SEMs of (g) pristine and (h) PDTCPD coated linen. (i) SEM of PDTCPD coated linen and corresponding sulfur (red) and carbon (grey) atom maps obtained using energy dispersive X-ray (EDX) spectroscopy. (j) SEM of PDTCPD coated carbon cloth and corresponding sulfur (red) and carbon (grey) atom maps. (k) Schematic of fabric coating using physical vapor transport (PVT). (l) Optical image and (m) SEM of linen coated with DTCPD using PVT (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

insoluble polymers [1,3]. We therefore focused our efforts on vapor printing PDTCPD onto topologically complex fabrics. Vapor printing is an especially advantageous method for creating PDTDPC films, as researchers have not been able to process CPD-containing polymers using conventional solution-based methods.

Fig. 3a-d shows optical images and scanning electron micrographs of both pristine and PDTCPD-coated linen and carbon cloth. Uncoated linen was distinctly white in color and turned burgundy when coated with PDTCPD. SEMs of pristine linen revealed the complex, multi-fibrillar surface of this prewoven fabric. The vapor printed PDTCPD film was uniform over the entire surface of the linen and hugged the micron-scale contours of each microfibril faultlessly. Accordingly, energy-dispersive X-ray (EDX) spectroscopy of PDTCPD coated linen revealed a uniform distribution of sulfur atoms (stemming from the vapor printed polymer) on the surface (Fig. 3i).

Uncoated carbon cloth looked dark grey to start and appeared black after vapor coating. The vapor printed PDTCPD film uniformly covered the entire circumference of each striated microfibril of the carbon cloth and, additionally, the microfibrils appeared to template the growth of the PDTCPD film so that striations were translated into the polymer coating as well (Fig. 3e-h). A cross-section SEM of freeze-shattered,

PDTCPD coated carbon cloth confirmed that the polymer uniformly coated the entire circumference of each fibril (Fig. 3j). EDX spectroscopy of this same surface unambiguously revealed that sulfur atoms were only present on the surfaces of each fibril, confirming that vapor printed PDTCPD films did not permeate into textile fibers and only formed conformal surface coatings.

In addition, we directly coated linen fabrics with the monomer DTCPD using the conceptually-simpler process of physical vapor transport (PVT). Using a singular monomer crucible placed in the reactor depicted in Fig. 1a, DTCPD was vaporized by heating and the resulting monomer plume was guided horizontally along the length of the reactor using a small flow (< 2 sccm) of nitrogen gas, thus coating linen substrates that were placed in the path of the monomer plume. A schematic of this process is depicted in Fig. 3k and an optical microscope image of a DTCPD coated linen fabric thus obtained is shown in Fig. 3l. While a vibrant blue color was observed on the linen swatch, small, white-colored discontinuities suggested that the coating was not uniform over the surface of linen. Coating nonuniformity was confirmed in SEMs of DTCPD coated linen (Fig. 3m), in which monomer aggregates were clearly evident, along with numerous uncoated areas that appeared brighter than the surrounding due to charging effects.

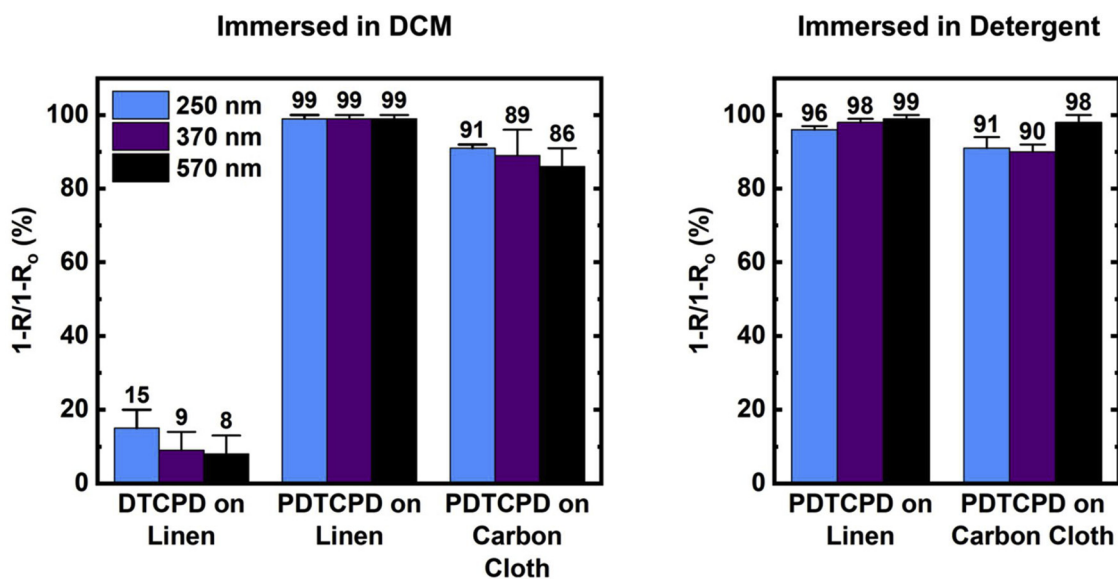


Fig. 4. Erosion of vapor-printed coatings on fabrics upon (a) rinsing with dichloromethane and (b) rinsing with commercial laundry detergent.

Previous work demonstrated the ability of vapor printed polymer films to resist delamination and erosion from textile substrates [21]. Therefore, the coated textile samples discussed above were immersed for 10 min in dichloromethane followed by a detergent solution (10% v/v). UV-vis spectra were recorded before and after immersion, with reflectance being monitored as a function of three separate wavelengths (250, 370, and 570 nm). The percent change in the 1-reflectance values after washing is plotted in Fig. 4. On average, samples coated with PDTCPD retained over 90% of their original values after being immersed in either an organic solvent or laundry detergent, confirming that reactive vapor printing affords mechanically robust coatings on fabrics. In contrast, the molecular DTCPD coating on linen created by PVT was nearly washed away by an organic solvent and completely washed away by laundry detergent (Figure S3). This result, and those of the images discussed above, suggested that reactive vapor printing is a particularly useful processing technique for creating cyclopentadienone-containing, *n*-dopable conjugated polymer films on textile substrates.

3. Conclusions

In summary, we vapor-printed an electron-accepting conjugated polymer by effecting the vapor phase oxidative polymerization reaction of a heavy, cyclopentadienone-containing monomer in a custom-built hot-wall reactor. The structure of the insoluble, vapor-printed polymer was probed by IR and UV-vis spectroscopy and the major structural features of the monomer were found to be retained post-polymerization. The measured band energy levels of the vapor printed polymer compared well with those of previously-investigated electron transporting materials. The vapor printed polymer films conformally coated topographically-complex fabric substrates, with minimal evident erosion after various rinsing procedures. These characteristics suggested that reactive vapor printing is a viable method for coating textiles with *n*-dopable conjugated polymers, providing a potential route to wearable optoelectronic devices that include monolithically-integrated active layers. Our future, follow-up efforts will expand on this preliminary work to build and characterize transistors and simple diodes incorporating our vapor printed polymer.

4. Experimental

4.1. Materials and general methods

All reagents were purchased through Sigma Aldrich and used without further purification unless otherwise stated. Dithienylcyclopentadienone (DTCPD) was synthesized following previous reports [22]. Ultraviolet-visible (UV-vis) spectra were collected using an Agilent 8453 spectrophotometer. The optical band gap E_{opt} of vapor-printed films were estimated by linear extrapolation from the absorption feature edge to baseline and subsequent conversion of the wavelength (nm) into energy value versus vacuum (eV). For vapor coated textile substrates, reflectance measurements were acquired with a Thermo Scientific Evolution 220 UV-vis Spectrophotometer with ISA 220 integrating sphere under reflectance and transmittance mode; the light beam was normal to the substrates. The reflectance of coated textiles was measured both before and after immersion, for 10 min, in either dichloromethane or a 10% by volume detergent solution. Attenuated total reflectance infrared spectroscopy (AT-IR) was conducted on a Bruker Alpha-p spectrophotometer. Film thicknesses were measured with an optical profilometer (Zygo NewView 7300, Veeco DekTak 150, and Veeco NT9080). Field-emission scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) spectroscopy were carried out with a Magellan 400 microscope. Ultraviolet photoelectron spectroscopy (UPS) was performed with an Omicron SPHERA hemispherical analyzer using a He I light source (21.2 eV). ITO-coated glass substrates to be analyzed with UPS were prepared via the following procedure: sonicate substrates in a detergent solution for 5 min, rinse with DI water and sonicate in acetone for 5 min, immerse into boiling isopropanol for 5 min (2x) and treat with UV-ozone for 30 min. The Fermi level of ITO thus prepared, as measured on our instrument, was 4.6 eV. The valence band edge of PDTCPD (-6.7 ± 0.2 eV) was calculated as the average of three separate samples with valence band edges measured at 6.86, 6.74, and 6.38 eV.

4.2. Reactive vapor printing of PDTCPD

Vapor phase polymerization of DTCPD was conducted in a custom-built tube-shaped quartz reactor. DTCPD monomer and iron (III) chloride ($FeCl_3$) oxidant were placed in tungsten and ceramic crucibles, respectively. The distances between the monomer crucible, vacuum outlet, and oxidant crucible were consistent for all polymerizations.

Substrates such as glass, ITO coated glass, linen fabric, and carbon cloth was placed between the reagent crucibles. The reactor was pumped down using an Edwards direct-drive vacuum pump and maintained at pressures between 100–200 mtorr using a nitrogen gas inlet. Resistive heating tapes were employed to heat two adjacent regions at 220°C and 175°C; consisting of monomer/substrate and oxidant, respectively. The oxidant region was heated 9 min before the monomer/substrate region, and the entire deposition, from when the oxidant began heating to when the heat was removed, lasted 32 min. After the deposition, PDTCPD films were rinsed with copious amounts of (1) methanol and (2) 10% by volume diisopropylamine in methanol to remove residual monomer and iron salts. EDS spectra (Figure S2) of PDTCPD films confirm the removal of all iron salts, consistent with previous reports [3,14,15,21].

4.3. Physical vapor transport of DTCPD

Physical vapor transport of DTCPD was conducted using the reactor discussed above. DTCPD was placed in a tungsten crucible. For all depositions, the distance between the crucible and vacuum outlet was 9 in.. Resistive heating tape was used to heat the monomer to 220°C, and linen substrates were placed outside the heating region. The chamber was pumped down via a vacuum and pressures were maintained at 100–200 mtorr using a nitrogen gas inlet. Additionally, the influx of nitrogen gas served to transport the monomer vapor outside the heating region, at which point the monomer would condense onto the linen substrates.

Conflict of interest

The authors declare no competing financial interests

Acknowledgments

This material is based upon work supported by the National Science Foundation under CHEM MSN1807743. T.L.A. also gratefully acknowledges support from the David and Lucile Packard Foundation.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.synthmet.2019.02.005>.

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