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CHARACTERIZATION OF Zn^{2+} -DOPED
POLY(VINYLIDENE DIFLUORIDE) FILMS BY X-RAY
PHOTOELECTRON SPECTROSCOPY

BY
ANGELA THACH

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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IN
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MASTER OF SCIENCE

OF

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2020

ABSTRACT

Thin films of fluorophores coated onto poly(vinylidene difluoride) (PVDF) substrates are reported to have enhanced photophysical properties. Zinc (II) has proven to be an effective dopant in these polymer films by further increasing the photophysical observations of the surface dye. These enhancements make for effective sensors when exposed to various analytes. Some studies of interfacial effects between the top atomic layer of these doped PVDF films and sensing dye layer have been investigated by focusing on absorbance and fluorescence spectroscopy of the dye, which lead to how the orientation of these dyes change from being a component of this bilayer. The focus has been primarily on understanding the dye component, then drawing conclusions on how the top PVDF layer may have led to these effects on these dyes. Instead, this thesis centers solely on understanding the chemical composition of the top 10 nm of these PVDF films and extrapolating how these findings may affect the phenomenon seen in the photophysical layer. With the use of X-ray photoelectron spectroscopy (XPS), elemental analysis has shown there is no additional coordination besides what had been previously reported of a tetragonally distorted six-coordinate Zn^{2+} complex with *N,N*-dimethylformamide (DMF) ligands. Signature pinhole formation has also been observed. Surface roughness profiles prove there is no change in surface roughness with an increase of Zn^{2+} doping. All lead to the conclusion that the only contributing factor in these doped PVDF films is the introduction of surface charging that suppresses aggregation and increases monomer formation of these dyes.

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PREFACE

The following thesis is presented in manuscript format. This manuscript has not yet been submitted for journal publication, but there is the intention to publish in *Langmuir*. Review will be conducted in the near future.

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MANUSCRIPT

Characterization of Zn²⁺-Doped Poly(vinylidene difluoride) by X-Ray Photoelectron
Spectroscopy

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The following is intended for submission in *Langmuir* and is presented here in
manuscript format.

INTRODUCTION

Modern, feasible methodologies have led to the formation of nanoscale poly(vinylidene difluoride) (PVDF) films with little time and cost.¹⁻⁶ In particular, these stand-alone thin films have wide applications in ferroelectricity and piezoelectricity.⁷⁻¹³ However, when sandwiched between a fluorescent dye layer and a substrate such as glass or silicon, PVDF has proven to enhance the photophysical behaviors of the dye compared to when the dye layer is not in conjunction with the polymer.^{14,15} Because the PVDF topographical layer has significant surface roughness, there is more area per unit of dye being deposited onto the PVDF. The roughness also adds for more internal reflection of any light source. These factors contribute to an increase in absorbance and emission intensities, allowing these multilayer components to act as effective sensors when exposed to a number of analytes. The use of fluorescent dyes in sensing materials has been widely studied,¹⁶⁻²⁵ and the increase in photophysical properties make them more susceptible to quenching in the presence of an analyte.

By varying the composition of these PVDF films, we can further improve the sensing performance of the multilayer system. In particular, metal doped thin films have been recently introduced, with increased performance in applications. Zinc (II), a very inexpensive, colorless, d¹⁰ transition metal cation has been doped in to PVDF thin films in the form of zinc (II) nitrate hexahydrate, and these additions led to an even further modulation of spectroscopic behavior compared to its non-doped counterpart. Analysis has been done on these Zn²⁺ doped PVDF films in terms of thickness, surface roughness,

and some chemical binding with infrared spectroscopy and thermogravimetric analysis (TGA). In particular, rhodamine 6G (Rh6G) has been paired as a top layer to these films. However, this previous study focused primarily on the photophysical changes of the Rh6G. Zn^{2+} exists in a tetragonally distorted 6-coordinate complex, bound to DMF ligands.²⁶ This dopant adds surface charge, creating an ion-dipole effect between the cation and the Rh6G, possibly inducing its increased emission intensity. The PVDF layer itself needs further investigation to fully understand what is happening at the interface with Rh6G, which is the objective of this study.

PVDF exists primarily in 3 different crystalline phases: α -, β -, γ - shown in Scheme 1.

Scheme 1. Crystalline phases of PVDF, with their different orientations of *trans* and *gauche*.

α -phase is nonpolar due to its antiparallel arrangement within its unit cell, canceling out the dipoles and making α -PVDF paraelectric. PVDF primarily exists in this phase. The β - and γ -phases are polar due to the orientation of its repeating units. In particular, the β -phase of PVDF has all s-*trans* sigma bonds, meaning the fluorine atoms

are all pointing in the same direction, enhancing its polarity, which increases its ferroelectric and piezoelectric properties.

Industrial and scalable methods of producing β -phase PVDF plastics have proven to be difficult, with some applications on stretching the plastic to increase tensile strength.^{27–29} This, however, is hard to achieve for PVDF on substrate materials, but spin-casting has been a cost-efficient solution to this problem.^{30,31} This method spins the PVDF deposited substrate so quickly that thin, flexible films can be manufactured in a matter of minutes. This also increases the amount of ferroelectric β -phase, which is ideal for making these multilayered sensors because there is already an induced electric field from adding a Zn^{2+} complex to the polymer.

Having more β -phase may enhance the field throughout the entirety of the Rh6G layer. With a stronger dipole effect, the more suppression of Rh6G aggregation occurs, enhancing the fraction of monomer excited states and increase in emission. Scheme 2 depicts the multilayered sensor that is the motivation of this study.

Scheme 2. Interface between the bottom layer of Rh6G and the top layer of PVDF.

Because some level of interpretation has been done on the Rh6G layer to understand the interfacial layer with PVDF, this work primarily focuses on the top 10 nm of the

polymer film to investigate what exactly is the chemical binding at this side of the interface to gain deeper knowledge of the whole. The primary focus is to find any additional evidence of coordination or interactions that may not have been previously reported that may also contribute to the photophysical phenomenon seen with Rh6G.

EXPERIMENTAL METHODS

Preparation of Zinc (II) Nitrate Doped PVDF Solutions

3 % w/v PVDF solutions were made in a solvent system of 9:1 % v/v acetone to DMF. These solutions were sonicated for 1.5 hours at 40 °C with an output power of 125 W. Silicon wafers were cut into 1.5 cm x 1 cm rectangles and sonicated in ethanol for 20 mins to properly cleanse the silicon before substrate use. The ethanol was replaced, and the substrates were sonicated an additional 2 times. These substrates were then sonicated in distilled water for 3 rinses, 20 minutes each, to remove any ethanol. Air was blown onto the silicon to allow them to dry.

The proper amounts of zinc (II) nitrate hexahydrate was added to achieve 0, 1, 2, 3, 4, 5 mole percentages of Zn^{2+} doped in according to the following equation:

$$x\% = \frac{\frac{m_{Zn(NO_3)_2 \cdot 6H_2O}}{297.49 \text{ g/mol}}}{\frac{m_{Zn(NO_3)_2 \cdot 6H_2O}}{297.49 \text{ g/mol}} + \frac{m_{PVDF}}{64.03 \text{ g/mol}}} \times 100\%$$

x% is the mol % of Zn^{2+} ; m = mass (g) weighed of the corresponding compound; 297.49 g/mol is the molecular weight of $Zn(NO_3)_2 \cdot 6H_2O$, and 64.03 g/mol is the molecular weight of PVDF.

After allowing the 3 % w/v PVDF solutions to sit until they reach room temperature, these calculated masses of $Zn(NO_3)_2 \cdot 6H_2O$ were added to each sample

vial. These solutions were sonicated for 2 minutes with no heat, also at 125 W of output power.

Formation of Metal Doped Thin Films

Using the Laurell Technologies WS-400B-6NPP/LITE Spin Processor, films were prepared on cleaned silicon substrates. The spin-coater was purged by dry nitrogen gas for 2 minutes to remove any moisture in the spin-coater; then 125 μL of each metal doped PVDF solution was deposited on the substrates. These samples were spun at 1200 rpm for 45 seconds, then annealed at 60 $^{\circ}\text{C}$ for 2 minutes to remove any residual acetone.

These samples were measured for thicknesses using a Filmetrics F40 Thin Film Analyzer. The surface topology and roughness measurements were determined using a Filmetrics 3D optical profilometer. IR spectra were also collected on attenuated total reflectance (ATR) using a PerkinElmer Spectrum 100. These samples were then placed in a vacuum oven to degas any remaining solvents for 48+ hours at 25 $^{\circ}\text{C}$. A Thermo Scientific X-ray photoelectron spectrometer was used for elemental analysis of the top 10 nm of each film, two different spot locations per film, with each spot size being an oval shape 400 μm x 700 μm in minor and major diameters, respectively. The elemental composition and spectra for carbon, fluorine, oxygen, zinc, and silicon were measured for each different mole percentage of Zn^{2+} doped PVDF film.

RESULTS AND DISCUSSION

In this study, the undoped and doped PVDF films were analyzed for thicknesses and elemental composition at the top nanometers of the surface. Thicknesses, surface profiles, and FTIR analysis were measured before any analysis was performed on the XPS. The thicknesses of these films were used to determine where the thinnest part of the film would be for the first measurement at 10 nm. The surface profiles imaged the surface morphology of these films. FTIR analysis was performed to identify the phase composition of the PVDF, the structure of the Zn^{2+} complex, and what other elemental components may exist in the film when measurements were performed on the XPS.

Section I: Thickness Measurements using Reflectance Microscopy

Using a Filmetrics F40 Thin Film Analyzer, thickness measurements of each sample of PVDF film are reported in Figure 1. Reflectance microscopy was the technique used with a spot size of 20 μm in diameter. A total of 6 measurements were taken of each film to report two different mean heights per film. Each mean height was calculated from 3 similar thickness measurements, and the errors were calculated from the standard deviation of the mean. Figure 1 shows that increasing the amount of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in each film does not have any noticeable change in film thickness when using the same spin-casting conditions. Initial analysis of the optical microscopy shows that PVDF films have significant differences in thickness depending on spot location. These variations are reported in two different categories of lower and higher elevation. As there is a greater

amount of Zn^{2+} -doping, the thickness measurements of PVDF are fairly consistent at ~400 nm for the higher elevated areas and ~300 nm for the lower elevated areas.

Figure 1. Thickness measurements of undoped and doped PVDF films, in two categories of lower and higher elevation of PVDF.

Section II: Surface Topology from 3D Profilometry

The following images in Figure 2 represent the surface topology from 3D profilometry. There are areas of higher and lower elevation, showing significant roughnesses of these films. The striping and color variation is indicative of this surface morphology. According to the scale bars, there is approximately a 100 nm difference between the higher measurements, imaged in white, compared to the lower surface topology measurements, imaged in red. This is in agreement with the results of the thicknesses found from the reflectance measurements.

It is important to note that the profilometer images randomly dispersed pinholes throughout all the sample types. Because the thin film analyzer has a spot size of 20 μm in diameter and reports numerical data from the averaging of one spot, these pinholes are so small that they were undetected by the F40 microscope recording. Atomic force microscopy (AFM) had been done on these films in previous work, but pinholes were not reported,²⁶ most likely because the resolution of the probe tip of the AFM was too large to resolve the presence of these holes. Some holes are not deep enough to penetrate down to the silicon substrate, evidenced in the yellow-orange holes, but some are deep enough to expose the silicon or the silicon dioxide layer. For the samples that have pinholes extended to 0 nm, these images can also provide some insight on thickness measurements, depending on the size of these holes and how many are imaged. Confirmation on how accurate these thicknesses are can be done by comparing the areas of higher and lower elevation to the ones reported in Figure 1. Figure 2 images mean heights at ~ 400 nm and ~ 300 nm, which agree with the mean heights reported from the F40 microscope.

4 Mol % Zn^{2+} PVDF

5 Mol % Zn^{2+} PVDF

Figure 2. 3D profilometry of undoped and doped PVDF films. Imaged are a top view, surface roughness profiles, and a scale bar for roughness measurements.

Section III. Roughness Measurements from Profilometry

From 3D profilometry, thicknesses were taken as mean heights with root-mean-squared (RMS) values as the error method, shown in Figure 3. These RMS values show there is approximately ± 80 nm from the mean height. These measurements are comparable to the thicknesses shown in Figure 1. Overall, there is no substantial change in thickness and surface roughness with the addition of more $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in each PVDF sample, meaning surface roughness is not a contributing factor in the photophysical changes between the doped thin films.

Figure 3. The average height measurements of each sample along with their root-mean-square (RMS) values as the errors.

Section IV: Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy has proven to be an accurate method not only in determining the elemental composition of polymer materials, but distinguishing their phase behavior as well.^{32–34} The IR spectra from Figure 4 correspond with previous reports of metal nitrate hexahydrate doped PVDF films.^{26,35} All overlaid spectra were normalized to the phase independent peak at 1171 cm⁻¹. Figure 4 highlights the three different phases: α -phase is present at 761 cm⁻¹, β -phase by the peak at 1277 cm⁻¹, and γ -phase at 1233 cm⁻¹. The β - and γ -phases are also represented at 841 cm⁻¹. Spin-casting is a simple, convenient method in enhancing the β -phase of the polymer while keeping the film thin and flexible. The increase in β -phase usually corresponds with a dual increase in γ -phase and decrease in α -phase, but the increase in baseline in the lower energy range for 3 and 5 mol % Zn²⁺ has resulted in the opposite effect. Nitrate has vibrational bands at 720 cm⁻¹ and 830 cm⁻¹,³⁶

which causes the apparent increase in absorbance of the peak corresponding to α -phase at higher amounts of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ addition.

Figure 4. Infrared spectrum of PVDF thin films with labeled phases at their corresponding wavenumbers (cm^{-1}).

Figure 5 is important in confirming the coordination of DMF to Zn^{2+} . Non-coordinated DMF has a vibrational peak at a higher energy than where carbonyl peaks appear in the Zn^{2+} -doped PVDF. Any noticeable acetone has been completely evaporated from these films from annealing procedures, and from allowing them to sit in the atmosphere and vacuum for several days. This shift in energy confirms that the DMF is coordinating with the Zn^{2+} . Previous work has shown the deconvolution of this carbonyl region to three peaks, two of which are representative of coordinated DMF at 1653 and 1642 cm^{-1} . The ratio of these peaks is approximately 2:1, suggesting a tetragonally distorted octahedral complex.²⁶

Figure 5. IR spectra of carbonyl region with indication of the carbonyl energies of acetone and uncoordinated DMF.

Scheme 3 depicts the proposed structure of this Zn^{2+} complex based on the conclusions from Figure 5.

Scheme 3. Proposed structure of tetragonally distorted $[\text{Zn}(\text{DMF})_6]^{2+}$.

This $[\text{Zn}(\text{DMF})_6]^{2+}$ complex is tetragonally distorted as seen in the shoulder region of the carbonyl peak and is resonance stabilized. The water molecules are not bound to the Zn^{2+} in these films and are embedded in the PVDF.

Figure 6 provides information on whether or not water may be retained by the time these films are analyzed by the XPS. There is a weak absorbance of an O-H band in the 5 mol % Zn^{2+} PVDF, suggesting the presence of H_2O or Si-OH. The water molecules would be from the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the Si-OH band would be indicative of surface Si-OH found in the pinholes of these films. Based on 3D profilometry of these films, the 5 mol % Zn^{2+} does have considerably more pinholes than the other films, suggesting no water is retained in any of these films by the time XPS analysis is performed.

Figure 6. The IR spectra of O-H bands present in the undoped and doped films.

Figure 7 focuses on the noticeable nitrate region within the IR spectra. Nitrate as a counterion usually appears at 1360 cm^{-1} as a very intense peak.³⁷ The slight shifts in energy around the 1340 cm^{-1} region are accounted for by hydrogen bonding of the nitrate oxygen atoms to the partially positive hydrogen atoms in the PVDF. Metal nitrate doped PVDF films have less intense nitrate bands, but the literature has proven that nitrate is retained in these films by following the same solution preparation in making these doped PVDF

solutions.³⁸ Figure 4 depicts an upward shift in baseline around the lower vibrational region due to the added nitrate bands at 720 and 830 cm^{-1} ,³⁷ also confirming nitrate retention within the films.

Figure 7. The IR region of nitrate present in undoped and doped PVDF, with indication of nitrate's wavenumber (cm^{-1}).

Section V: XPS Analysis

XPS has been a widely used instrumental technique in characterizing the elemental composition of PVDF films.^{39–41} Survey scans of the undoped and 5 mol % Zn^{2+} doped PVDF are shown in Figure 8. In the absence of Zn^{2+} , the spectrum shows prominent features in the carbon 1s and fluorine 1s binding energy regions, as expected. An additional feature not characteristic of PVDF is the presence of oxygen. As shown in the inset, the

detection of oxygen must arise from SiO_2 on the surface of the substrate. This is in agreement with the observations from 3D profilometry. Even though these films average 350 nm in thickness, some pinholes extend to the silicon substrate. Because it is known that the survey scan measured at the top 10 nm, the detection of SiO_2 at this penetration depth support this conclusion.

In the 5 mol % Zn^{2+} PVDF, the spectrum depicts highly intense features pertaining to the fluorine and carbon atoms of PVDF, as expected. There is a noticeable decrease in the F1s peak intensity, which is also expected at this higher mole percentage of Zn^{2+} doping. At ~ 1030 eV, there are two, relatively less intense peaks indicating the presence of zinc. Because $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to this film, there should be a corresponding signal in the O1s region at ~ 530 eV. The spectrum shows a relatively more intense peak pertaining to oxygen compared to the undoped PVDF. This demonstrates that the presence of nitrate is being detected. According to the FTIR analysis, no water remains within these films, meaning the increase in O1s intensity is not due to the addition of more hydrate molecules. From the FTIR carbonyl region, there is DMF coordinating to Zn^{2+} , meaning that there is an expected oxygen contribution from DMF in the O1s signal. Referring to the Si2p inset, there are two weakly resolved peaks, as opposed to the 0 mol % Zn^{2+} PVDF spectrum which shows only one peak. Not only does this suggest the presence of pinholes, but it shows the beam has penetrated through the SiO_2 layer to the silicon layer, which is indicative of the second peak at ~ 99 eV. In reference to the O1s peak, there is some oxygen contribution from the SiO_2 , but more so from the additional nitrate and DMF that is retained in the doped films.

Figure 8. Survey scans of an (A) undoped and (B) 5 mol % Zn²⁺-doped PVDF film with peak labels for all the analyzed elements.

Table 1 analyzes the atomic percentages of the elements detected from the survey scans and what the theoretical percentages would be. Table 1A highlights the theoretical atomic percentages of each sample, assuming no presence of pinholes, which would

contribute increases in the oxygen and silicon detection. DMF is retained in 1-5 mol % Zn^{2+} PVDF samples, so these calculations were done under the assumption that 6 DMF ligands are bound to one Zn^{2+} in PVDF, along with the PVDF contribution. These are also done according to the FTIR in Figure 6 that no water is being retained in any of these films.

There should be an overall decrease in atomic percentages of carbon and fluorine, with increases in oxygen and zinc as more $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ has been added. The undoped PVDF still reports the highest atomic percentages for carbon and fluorine, as expected. 5 mol % Zn^{2+} PVDF also has the lowest percentage of fluorine, also as expected. There is most likely some unknown external carbon source at varying amounts being detected, which is why there is a fluctuation in the carbon atomic percentages, which causes fluctuations in the fluorine percentages. The oxygen percentages seem to be following an expected increasing trend as more nitrate is being added, and more DMF is coordinating with increasing mol % Zn^{2+} . There is no substantial silicon percentage detected for 0-4 mol % Zn^{2+} , but based on Figure 8, pinholes are detected at 0 and 5 mol % doped PVDF. This suggests the Si2p signal in the undoped PVDF was unable to be resolved by the XPS, which has an error of $\pm 1\%$. As for the Zn%, there is no expected increase as Zn^{2+} doping increases, suggesting the surface composition is different than the bulk of the films.

(A)					
Theoretical Atomic Percentages					
Mol % Zn²⁺	C1s	F1s	O1s	Si2p	Zn2p
0	37.5%	59.4%	0%	---	0%
1	36.9%	58.4%	3.0%	---	1.0%
2	35.3%	55.8%	5.6%	---	1.9%
3	33.8%	53.5%	8.1%	---	2.8%
4	32.4%	51.3%	10.4%	---	3.6%
5	31.2%	49.3%	12.5%	---	4.3%

(B)					
Experimental Atomic Percentages					
Mol % Zn²⁺	C1s	F1s	O1s	Si2p	Zn2p
0	50%	49%	1%	---	0%
1	50%	44%	4%	---	2%
2	50%	47%	2%	---	1%
3	49%	49%	2%	---	1%
4	48%	49%	2%	---	1%
5	49%	45%	3%	1%	1%

Table 1. (A) Theoretical atomic percentages of 0-5 Mol % Zn²⁺ PVDF. (B) Reported atomic percentages of 0-5 mol % Zn²⁺ PVDF, all with an uncertainty of $\pm 1\%$.

The silicon XPS spectra provides insight of the presence of pinholes that may contribute to the deviation of the reported atomic percentages from the calculated ones.

Figure 9 implies there are pinholes within our polymer films following normal spin-casting parameters and sonication times. One reason as to why this may occur is that the spin-casting acceleration is so fast that some of the solution is spun off the substrate. Future studies will involve decreasing spin-casting speeds and time adjustments for this issue. A more likely reason may be the presence of hydrofluoric acid within the solution itself. Extensive sonication of the PVDF solutions during preparation may lead to the formation of HF, which can etch layers of the PVDF at localized areas to expose the SiO₂ layer, or it can etch even further into the SiO₂ layer, exposing the silicon substrate itself.

The evidence of HF formation is apparent when referencing Figures 9A, 9D, and 9E. Figure 9D shows the Si2p spectrum of an undoped PVDF film that was prepped from a solution that sonicated at 3 hr. at 40°C. Figure 9E shows the spectrum of a 5 mol % Zn²⁺ PVDF film prepped from a solution of the same increased sonication time, but with an additional 30 min sonication after the addition of Zn(NO₃)₂·6H₂O. By comparing these two figures with the spectrum of the plain silicon, it is determined that sonication of the PVDF solution prior to metal doping has no significant effect on the number of pinholes formed in the films. Only in the doped films is there a noticeable peak relating to silicon, meaning the Zn²⁺ catalyzes more HF formation to penetrate beyond the SiO₂ layer to the substrate. The longer sonication times only after metal doping show more silicon substrate exposure, meaning some compound is being produced that is cleaning the surface. HF is the most likely cause of this problem.

Scheme 4. Possible products from the loss of HF from PVDF.

Scheme 4 is adapted from previous literature work on metal catalysts and HF formation effects on PVDF.⁴² Once the PVDF solution is deposited onto the substrate and we allow the sample to spin-coat, HF is displacing some of this PVDF and SiO₂ layer before it evaporates into the atmosphere. This reaction is depicted in Scheme 5.

Scheme 5. The reaction of HF and SiO₂ that exposes the silicon substrate.

These reactions suggest there is inhomogeneity within the PVDF film, which may explain some of the fluctuations observed in the reported atomic percentages.

Figure 9. Silicon 2p spectra of the following films or substrates: (A) Plain silicon with no PVDF layer, (B) undoped PVDF sonicated following normal sonication times, (C) 5 mol % Zn^{2+} PVDF, following normal sonication times, (D) 0 mol % Zn^{2+} PVDF with 3 hr. sonication, and (E) 5 mol % Zn^{2+} PVDF with 3 hr. sonication, followed by 30 min sonication of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Any silicon detection will result in the loss of some quantitative measurements of carbon, fluorine, and zinc. The presence of SiO_2 will add another contributing factor to the O_{1s} spectra, but these intensities will fluctuate depending on the amount of silicon substrate detected at each spot, and consequently how much nitrate detection is lost.

Although some fluorine composition may be lost due to HF formation and its effects on the silicon, the F1s peak is still the most prominent peak by far in comparison to the other peak intensities. Figure 10 displays the F1s spectra for undoped and 5 mol % Zn^{2+} doped PVDF. Fluorine has the highest product of photoionization cross section and kinetic energy compared to the other analyzed elements, meaning the F1s spectra display the highest intensities at their intrinsic binding energies. The binding of fluorine atoms within this peak are reported in Table 2.

All undoped and doped PVDF F1s spectra were deconvoluted to 2 Gaussian peaks, meaning no additional growth of new fluorine binding occurs when additional Zn^{2+} is in these films. All peak assignments were referenced from the NIST database.⁴³ There is the expected major contribution of C-F from $(\text{CH}_2\text{-CF}_2)_n$ at ~ 688.0 eV. There is a minor peak at a slightly higher binding energy of ~ 688.4 eV, which is attributed to the small amount of PVDF that has polymerized to the $(\text{CF}_2\text{-CF}_2)$ bond formation instead of its conventional one. Having a $-\text{CF}_2$ group bound to another $-\text{CF}_2$ as opposed to $-\text{CH}_2$ would have a higher binding energy because it is more to a more electronegative group.

Figure 10. Fluorine 1s spectra of an (A) undoped and a (B) 5 mol % Zn^{2+} doped PVDF thin film, along with their fits and component peaks.

Peak	Binding Energy (eV)	Γ (eV)
C-F	688.03 $\pm$ 0.04	0.851 $\pm$ 0.007
<u>F₂C-CF₂</u>	688.40 $\pm$ 0.03	1.79 $\pm$ 0.02

Table 2. Deconvoluted XPS peaks for fluorine 1s spectra. Displayed are the binding energies for each respective peak, full widths at height maximum (FWHM, Γ), and standard deviations of each value.

Figure 11 displays the C1s spectra of 0 and 5 mol % Zn²⁺ PVDF. Based on the F1s spectra from Figure 10, it is expected that there is an intense peak attributed to the C-F bonding in PVDF. There are two highly intense peaks at ~286 eV and ~291 eV, with an adventitious shoulder at ~285 eV. To further investigate the elemental components that contribute to these spectra, Table 3 shows the deconvolutions averaged from each C1s spectra of 0-5 mol % Zn²⁺ PVDF films.

All peak assignments were referenced from the NIST database.⁴⁴ The C1s distribution for undoped and doped PVDF was deconvoluted to 5 Gaussian peaks. Known from the FTIR spectra in Figure 5, there is no acetone retention in any of these films and no DMF retention in the undoped PVDF film, but the C1s deconvolution shows the presence of residual solvent. The 5 distinct peaks are representative of the carbon bonding shown in Table 3, with the corresponding binding energies and full FWHM. Carbon bound to fluorine, which only exists in the PVDF, is found at the highest binding energy due to fluorine's strong electronegativity. The second most noticeable peak at ~286 eV is mostly representative of the C-H bonding in PVDF. The peak intensities match the correspondence of carbon functional group to binding energy because the mole ratio of C-F:C-H in PVDF is 1:1. The C=C shoulder at ~285 eV is from the dehydrofluorination of carbons within the

PVDF due to HF formation. From Figure 9, we know HF has formed and created pinholes within this analysis spot. This also means that the area should have some amount of alkene carbons that were bound to the fluorine and hydrogen atoms that converted to HF after increased thermal conditions during prolonged sonication. Because the silicon substrate was not detected from Figure 9B, this shoulder is not as prominent as the one in the C1s 5 mol % Zn^{2+} PVDF, where enough HF was produced to penetrate past the SiO_2 layer for Si detection.

Overall, undoped films have a N-C=O peak and N-C-H peak from DMF being retained, which shows that the FTIR was unable to resolve this residual solvent. The growth of these peaks with increased doping confirms the coordination of DMF to Zn^{2+} . When comparing the relative areas of the deconvoluted peaks, the ratio of C-H (PVDF) to N-C=O (DMF) is approximately 2:1, adding further confirmation that the DMF ligands are bound to the Zn^{2+} in a 6-coordinate tetragonally distorted complex. The ratio of C-F to C=C is relatively large at 12:1 in the undoped PVDF film, but is much smaller at 4:1 in the 5 mol % Zn^{2+} . Suggested from Scheme 4, more alkene carbons are being produced as more HF is being catalyzed from the increased doping of Zn^{2+} .

Figure 11. Carbon 1s spectra of an (A) undoped and a (B) 5 mol % Zn^{2+} -doped PVDF thin film, along with their fits, and component peaks.

Peak	Binding Energy (eV)	Γ (eV)
Contamination & $\text{sp}^2 \text{C}=\text{C}$ (PVDF)	285.1 ± 0.3	0.71 ± 0.05
$\text{sp}^3 \text{C}-\text{H}$ (PVDF)	286.5 ± 0.2	0.7 ± 0.1
N- $\text{C}-\text{H}$ (DMF)	286.7 ± 0.2	0.7 ± 0.1
N- $\text{C}=\text{O}$ (DMF)	290.4 ± 0.2	1.9 ± 0.1
$\text{C}-\text{F}$ (PVDF)	290.96 ± 0.02	0.60 ± 0.02

Table 3. Deconvoluted XPS peaks for carbon 1s spectra. Displayed are the binding energies for each respective peak, full widths at height maximum (FWHM, Γ), and standard deviations of each value.

The O1s spectra were then analyzed in Figure 12 and Table 4. The undoped PVDF O1s spectrum was almost entirely attributed to SiO_2 . Any SiO_2 contribution was unresolved in the deconvolutions for the doped PVDF samples, and there were hardly any statistical values for H_2O being retained, which is consistent with the FTIR findings. This means the only constant oxygen contributions in each sample are the ones from the nitrate and DMF. The oxygen atoms in nitrate are bound directly to nitrogen, which are relatively close in electronegativities, meaning this functional group is at higher binding energies compared to the oxygen in the carbonyl group of DMF. This DMF peak was deconvoluted to 532.3 ± 0.3 eV, which is between the literature binding energies representative of ZnO at 530.2 eV and the oxygen of an amide group, which is at 532.9 eV.^{45,46} This means the DMF is coordinating with the Zn^{2+} , causing it to shift higher relative to the ZnO binding energy, and lower compared to the literature binding energy of an amide.

Because there is no O1s peak at 530.2 eV, no ZnO exists within these films. This is important to note because ZnO formation would result in the loss of $[\text{Zn}(\text{DMF})_6]^{2+}$. Literature findings report that sonication at 100 W and 150 W power output form ZnO after 30 minutes and 40 minutes, respectively,^{47–49} which is about ten times the duration of sonication used to dissolve the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Figure 12. Oxygen 1s spectra of an (A) undoped and (B) 5 mol % Zn^{2+} -doped PVDF film, along with their fits and component peaks.

Peak	Binding Energy (eV)	Γ (eV)
N-C= <u>O</u> -Zn ²⁺	532.3 $\pm$ 0.3	0.8 $\pm$ 0.1
N- <u>O</u> (Bond Order = 1.5)	533.4 $\pm$ 0.5	1.1 $\pm$ 0.1

Table 4. Deconvoluted XPS peaks for oxygen 1s spectra, with their respective binding energies, FWHM (Γ), and standard deviations of each value.

Figure 13 depicts representative Zn2p spectra in undoped and 5 mol % Zn²⁺ doped PVDF. All Zn2p spectra measured from doped films were deconvoluted to 3 Gaussian peaks. Spin-orbit coupling results in two noticeable peaks, representative of Zn 2p_{1/2} and Zn 2p_{3/2}, with approximately 23 eV separation. Deconvolutions show slight asymmetry in the Zn2p_{3/2} peak, suggesting the presence of some coordinated Zn²⁺ species. ZnO typically has a Zn2p signal at 1021.4 eV,⁵⁰ but Zn²⁺ bound to DMF would have a slightly higher binding energy due to the electronegative groups of DMF. This is why the deconvoluted Zn-O peaks are located slightly above 1022 eV. In addition to the shift in wavenumber of carbonyl DMF from Figure 5, the growth of a N-C=O peak from the C1s spectra of Figure 11, and the growth of a carbonyl peak from O1s spectra in Figure 12, there are multiple pieces of evidence that the DMF is coordinating with the Zn²⁺.

There are no noticeable trends in relative peak areas of the Zn2p spectra as Zn²⁺ doping increases, which agrees with the reported atomic percentages from Table 1B. This leads to the conclusion that these films are relatively consistent in their Zn²⁺ composition at the top 10 nanometers.

Figure 13. Zinc 2p spectra of an (A) undoped and a (B) 5 mol % Zn^{2+} -doped PVDF film, along with their fits and component peaks.

Peak	Binding Energy (eV)	Γ (eV)
<u>Zn</u> -O (DMF) of Zn2p_{3/2}	1022.2 ± 0.6	1.5 ± 0.3
<u>Zn</u> -O (DMF) of Zn2p_{3/2}	1022.6 ± 0.1	0.78 ± 0.08
Zn2p_{1/2}	1045.8 ± 0.1	1.02 ± 0.05

Table 5. Deconvoluted XPS peaks for zinc 2p spectra. These were fit to 3 Gaussian peaks with their respective binding energies, and their FWHM (Γ), and standard deviations of each value.

Conclusion

These Zn^{2+} - doped thin films have significant surface roughness. Profiles of surface morphology show there is no observable change when adding more $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to these films. They also agree with the conclusions from the XPS analysis that pinholes exist within these films, most likely from HF formation that is catalyzed by the addition of Zn^{2+} . The XPS data at the top 10 nm and the FTIR spectra correspond well with each other, proving what had been previously been reported about how the Zn^{2+} interacts within the PVDF. DMF binds in a tetragonally distorted octahedral complex with Zn^{2+} , previously shown from the distorted carbonyl peak in the IR spectrum, but now from the relative deconvoluted peak areas of the C1s correspond with the 2:1 ratio of coordinated DMF, and the peak assignments of Zn-DMF bonding in O1s and Zn2p spectra.

Suggested by the atomic percentages reported, Zn^{2+} may have a preferential distribution, either in the bulk or on the surface of the film. Because Zn % did not increase with increasing Zn^{2+} doping, there is the possibility of Zn^{2+} preferentially diffusing into the bulk of the film. Under the assumption there is doping saturation at the surface, there is still enough Zn^{2+} in the bulk to have enhanced β -phase behavior. Future studies involve more analysis of these pinholes to see whether their presence contributes to the enhancement of spectroscopic behavior of dyes. There is a possibility that the $[\text{Zn}(\text{DMF})_6]^{2+}$ complex clusters at these pinholes, which would increase the induced electric field exhibited from this complex in these localized areas. Under the assumption that the $[\text{Zn}(\text{DMF})_6]^{2+}$ complex culminates in these pits, freeze fracturing the surface and

obtaining SEM images would be necessary. Pinhole defects are common in polymer samples,^{51,52} but the causes are not as widely studied. This signature pinhole formation specifically from the presence of HF is being newly reported in this work. Elimination of these pinholes would provide more uniformity to these films, which would provide more accurate atomic percentages. More importantly, depth profiling of these films must be successfully done to better understand the bulk, but methods to overcome charging effects from Zn^{2+} and thicker films must be used to obtain more accurate atomic percentages per layer etched.

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APPENDIX

Supporting Information

Figure S1. The following spectra were collected from a 1 mol % Zn^{2+} PVDF film: (A) C1s (B) F1s (C) O1s (D) Si2p (E) Zn2p (F) Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in (F).

Figure S2. The following spectra were collected from a 2 mol % Zn^{2+} PVDF film: **(A)** C1s **(B)** F1s **(C)** O1s **(D)** Si2p **(E)** Zn2p **(F)** Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in **(F)**.

Figure S3. The following spectra were collected from a 3 mol % Zn^{2+} PVDF film: (A) C1s (B) F1s (C) O1s (D) Si2p (E) Zn2p (F) Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in (F).

Figure S4. The following spectra were collected from a 4 mol % Zn²⁺ PVDF film: (A) C1s (B) F1s (C) O1s (D) Si2p (E) Zn2p (F) Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in (F).

Figure S5. The following spectra were collected from a 0 mol % Zn^{2+} PVDF film prepared from a 3-hr. sonicated solution: **(A)** C1s **(B)** F1s **(C)** O1s **(D)** Si2p **(E)** Zn2p **(F)** Survey scan. Spectral fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in **(F)**.

Figure S6. The following spectra were collected from a 1 mol % Zn^{2+} PVDF film prepared from a solution sonicated in a total of 3.5-hr.: (A) C1s (B) F1s (C) O1s (D) Si2p (E) Zn2p (F) Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in (F).

Figure S7. The following spectra were collected from a 2 mol % Zn^{2+} PVDF film prepared from a solution that sonicated for a total of 3.5 hr.: (A) C1s (B) F1s (C) O1s (D) Si2p (E) Zn2p (F) Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in (F).

Figure S8. The following spectra were collected from a 3 mol % Zn^{2+} PVDF film prepared from a solution that sonicated for a total of 3.5 hr.: **(A)** C1s **(B)** F1s **(C)** O1s **(D)** Si2p **(E)** Zn2p **(F)** Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in **(F)**.

Figure S9. The following spectra were collected from a 4 mol % Zn^{2+} PVDF film prepared from a solution that sonicated for a total of 3.5 hr.: (A) C1s (B) F1s (C) O1s (D) Si2p (E) Zn2p (F) Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in (F).

Figure S10. The following spectra were collected from a 5 mol % Zn²⁺ PVDF film prepared from a solution that sonicated for a total of 3.5 hr.: **(A)** C1s **(B)** F1s **(C)** O1s **(D)** Si2p **(E)** Zn2p **(F)** Survey scan. Fits and deconvoluted peaks are shown with their corresponding binding energies (eV) and FWHM (eV). Atomic percentages are included in **(F)**.