



Synthesis and Characterization of Cross-linkable Viologen Derivatives

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Abstract – In this study, crosslinkable allyl functional viologen derivative (ALV-Br) was synthesized with 4-4'-bipyridyl in the presence of allyl bromide in acetonitrile and the precipitated product was separated by filtration. Chemical characterization of the obtained structure was carried out as a result of FT-IR and ¹H-NMR spectra. In the cyclic voltammetry (CV) measurements performed for electrochemical characterization, a two-step reversible reduction peak attributed to viologen salts was clearly observed in the 0-0.8 V range. According to the UV-Vis absorption spectra, it is seen that they only absorb in the UV region below 400 nm in both solution and thin film. Thin films of ALV-Br salt were then spray coated in the presence of a tetrathiol-based crosslinker (pentaerythritol tetrakis(3-mercapto-propionate). In the final step, the surface morphology of the crosslinked thin film was examined by Atomic force microscopy (AFM) and compared with the results of the non-crosslinked one. Finally, the patterned film of ALV-Br could be obtained by this technique.

Keywords – Cross-linked film, DFT, surface morphology, thiol-ene click chemistry, viologens

1. Introduction

Thiol-ene click chemistry is a type of reaction that is commonly used in the preparation of thin films. This reaction involves the reaction of a thiol (a molecule with a sulfur-hydrogen bond) with an alkene (a molecule with a carbon-carbon double bond) in the presence of a photoinitiator or other catalyst (Hoyle & Bowman, 2010). When used in the preparation of thin films, thiol-ene click chemistry allows for the creation of highly cross-linked polymer networks with excellent mechanical properties. This is because the thiol-ene reaction can be performed under mild conditions (such as room temperature and ambient pressure), and it produces a highly efficient and selective reaction (Liu & Boyer, 2017). Thin films prepared using thiol-ene click chemistry can be used in a wide range of applications, including coatings, adhesives, and biomedical devices. The resulting films are highly durable, resistant to wear and tear, and have excellent adhesive properties (Killops et al., 2008). Overall, thiol-ene click chemistry is a powerful tool for the preparation of thin films, and it offers numerous advantages over other types of chemical reactions. By using this approach, researchers can create high-quality films that are both mechanically robust and chemically stable (Lowe et al., 2010).

The 1,1'-disubstituted-4,4'-bipyridinium salts known as viologens are by far the small molecule-based especially electrochromic materials that have received the greatest attention from both academic and industrial researchers. The main benefits of these materials are their high coloration efficiency, redox stability, ease of molecular design, and feasibility for large-area preparation. Electrochromism is called reversible optical changes that occur on a material when a low potential is applied to that material. Electrochromic films can be used on windows in buildings, on mirrors in cars, to obtain a safe drive by adjusting the amount of light

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intensity, as an active optical filter, in sunglasses, on traffic sign boards or on dashboards (Bange, 1999; Doyranlı et al., 2022; Gu et al., 2022; Wang et al., 2018). Scientists have focused on the research of organic materials, which could be an alternative to semiconductor technology, especially after the 1980s (Bronstein et al., 2020). Organic small molecules, viologens consist of the two pyridine rings and have the three reversible redox states (Vinh Quy et al., 2022) (Figure 1).

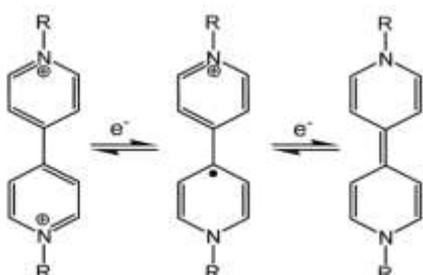


Figure 1. The three reversible redox states of viologens

There are important studies in the literature on viologens. Kim et al. attached phosphonate viologen (bis(2-phosphonoethyl)-4-4'bipyridinium dibromide) to the surfaces of 7.15 and 30 nm TiO₂ particles in order to investigate the effects on the performance of the electrochromic device in 2007. They found that the device exhibited high optical transparency and contrast ratio while being the slowest in terms of switching response (Kim et al., 2007). Moon et al. added methyl viologen and ferrocene as redox molecules to the gel electrolyte consisting of SMS (polystyrene-block-polymethylmethacrylate-block-polystyrene) and [EMI][TFSI] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). When the voltage was increased above 0.7 V, dark blue color was observed. It had good stability and a coloration efficiency of 105 cm² C⁻¹. In this way, it has been shown that functionality could be increased in ion gels with simple solution processes at a potential below 1 V in electrochromic devices (Moon et al., 2014). In another study by Oh et al. in 2017, dimethyl ferrocene (dmFc) was added into the gel being used as an anodic species. Multi-colored electrochromic devices based on flexible ion gels consisting of the two electrochromic materials (monoheptyl viologen (MHV⁺), diheptyl viologen (DHV²⁺) and copolymer for the electrolyte layer and ionic liquids were prepared. While both devices had a yellowish color in the bleached state, magenta and blue color were observed in the devices containing MHV⁺ and DHV²⁺ in the colored state, respectively. Moreover, while their coloration efficiencies were 87.5 cm² C⁻¹ and required a power of 248 μW/cm² to maintain the colored state for magenta; 91.3 cm² C⁻¹, required a power of 72 μW/cm² to maintain the colored state for blue color. These results show that multicolored ion gel-based electrochromic devices are quite advantageous (Oh et al., 2017). In 2019, some optimization studies were conducted by Madasamy et al. to increase the device performance. The effect of adding the complementary redox species or conjugated polymers to the appropriate electrochromic counter electrode materials on viologens had been studied and as a result, positive effects on the device performance were observed (Madasamy et al., 2019). When the literature is examined, it has been seen that viologens are very attractive because they are organic electrochromes, molecular designs can be made easily, and their color scales are wide. However, there may also be problems such as not short enough response times or stability problems. In this work, optimization studies were carried out by cross-linking of viologen salts to overcome the problems mentioned in the previous studies. Moreover, thanks to the patterned films to be made with this technique, the thin films can be obtained, especially in screen technology.

2. Materials and Methods

In the experiments, 4, 4' bipyridyl, allyl bromide, methanol (CH₃OH), dimethylformamide (DMF), acetonitrile (ACN), tetrabutylammoniumhexafluorophosphate (TBAPF₆), pentaerythritol tetrakis(3-mercaptopropionate) and chloroform was purchased from the Merck and Aldrich chemical company. Tetramethyl silane was used as an internal standard in ¹H-NMR spectra obtained in DMSO-d₆ at 400 MHz (JEOL ECX-400). The Cary 630 FTIR Spectrometer (Agilent Technologies) was used to measure Fourier transform infrared spectra (FT-IR) utilizing an attenuated total reflectance (ATR) module (4000-650 cm⁻¹). We investigated the electrochemical characteristics using a CH Instrument 617D potentiostat-galvanostat

system. In the electrochemical cell, reference, counter, and working electrodes were made of Ag wire, Pt wire, and glassy carbon, respectively. Tetrabutylammonium hexafluorophosphate (TBAPF₆) in CAN (0.1 mol L⁻¹) was used as the supporting electrolyte. The measurements were performed by using the cyclic voltammetry technique (CV) in an argon atmosphere. Analytic Jena-Speedcord S-600 diode-array spectrophotometer was used to evaluate the UV-Vis absorption spectra of the ALV-Br and ALV-BrX thin films between 300 and 1100 nm. Gaussian 09 was used for theoretical calculations, and GaussView 5.0 was used for visualization. The geometry optimization of the structures was carried out using the DFT method PM6 basis set functional coupled with B3LYP. Atomic Force Microscopy was used to examine the morphology of the thin film of ALV-Br and ALV-BrX (AFM, Nanosurf Naio). A measuring area of 10 μm × 10 μm was used for the non-contact mode at AFM measurements.

2.1. Synthesis of Allyl Viologen Bromide Salt (ALV-Br)

First, 4,4' bipyridyl (2 g, 12.80 mmol), allyl bromide (4.69 g, 30.00 mol) and ACN (100 mL) were taken into a balloon and kept at 80°C for 24 hours. Initially, the colour of the mixture turned into from colorless to yellow-orange, then orange color remained during the reaction (Figure 2). When the reaction time was over, the precipitated product was filtered with a sintered funnel and dried in a vacuum oven at 40°C to obtain the ALV-Br powder (Yield: 88%). FT-IR wavenumber (cm⁻¹): 3120, 3086 (C-H allyl); 3036 (C-H aromatic); 2986 (C-H aliphatic); 1622 (C=N); 1496 (C-C phenyl); 1170 (C-N); 1188 (C-N); ¹H-NMR (DMSO-d₆): 9.38, (d, 4H, Ar-Hb); 8.33, (d, 4H, Ar-Ha); 6.21 (m, 2H, Hd); 5.52, (d, 4H, He); 5.40, (d, 4H, Hc) (Figure 2).

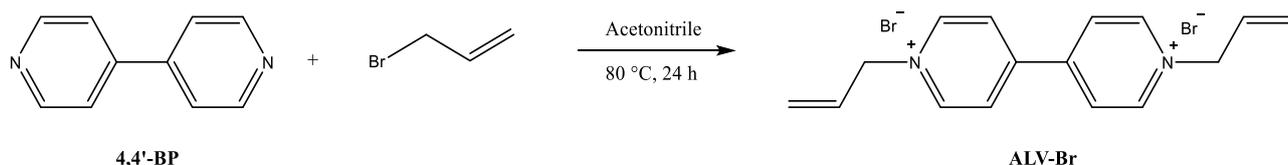


Figure 2. Synthetic pathway for ALV-Br

2.2. Preparation of Thin Films of Allyl Viologen Measurements

A crucial step in producing high-quality thin film coatings is cleaning the substrate. In this manner, the 2.5 cm × 2.5 cm glass substrates were washed for 15 minutes in the ultrasonic bath with water, acetone, and isopropyl alcohol (IPA), respectively. They were then dried at 40°C in a vacuum oven, and finally, to achieve molecular level cleaning, they were hold on for 30 minutes under the UV-ozone cleaner. To obtain the ALV-Br thin film, spray coating procedure was carried out 12 coating cycles and 70 °C plate temperature under 4 mbar pressure. After optimization of the thin film preparation, cross-linked film of ALV-Br (ALV-BrX) was prepared in the presence of tetrathiol-derived crosslinker (pentaerythritol tetrakis(3-mercapto-propionate) by applying similar procedure (Figure 3).

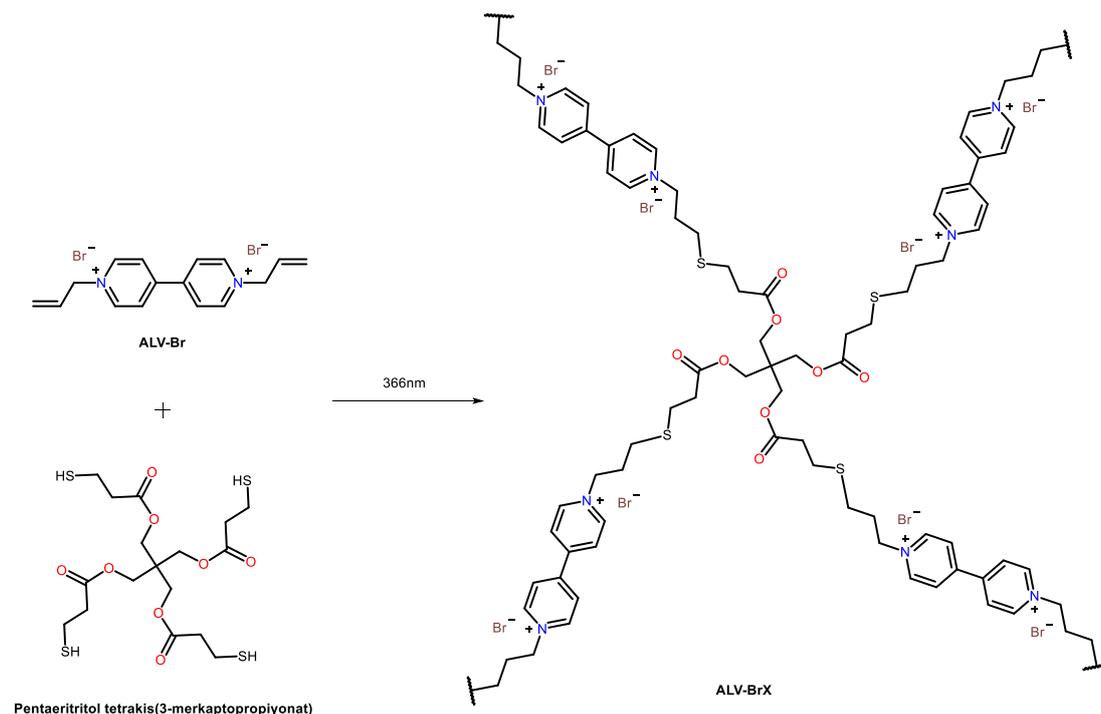


Figure 3. Synthetic pathway of ALV-BrX

To prepare the cross-linked ALV-BrX film, 50 mg of ALV-Br was added to 10 mL of DMF and the mixture saturated with the Argon gas was stirred at room temperature for 30 minutes to dissolve ALV-Br in the mixture. The filtered solution was coated on a 2.5 cm x 2.5 cm glass substrate surface using the spray coating method, with the addition of pentaerythritol tetrakis(3-mercapto-propionate) (38.5 μ L) as a crosslinker. Afterwards, cross-linking process was carried out on the film surface, which was maintained under 366 nm 100 W UV light for 15 minutes. Finally, the cross-linked ALV-Br film was washed with chloroform, acetonitrile and methanol, respectively in order to remove unreacted impurities from the film surface. When the similar procedure was performed using the mask, a 1 mm² patterned ALV-BrX film was obtained (Figure 4).

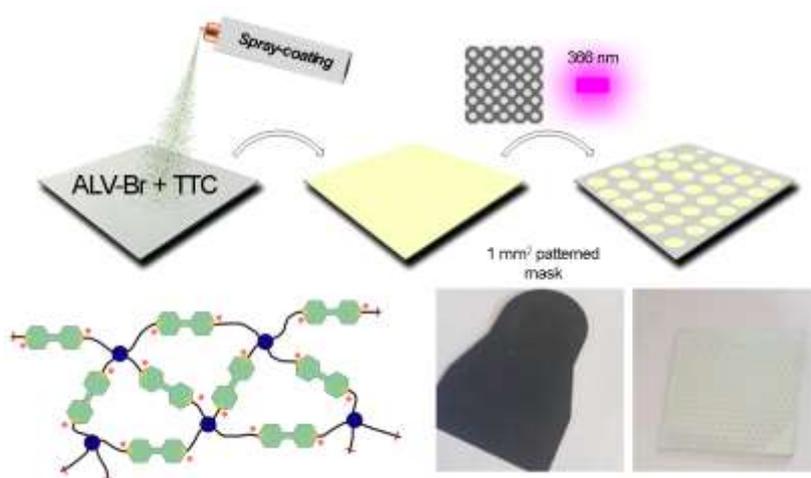


Figure 4. Crosslinking process of ALV-BrX film

3. Results and Discussion

3.1. Synthesis and Characterization

The synthesis of ALV-Br was carried out by refluxing 4,4'-Bipyridyl and allyl bromide in acetonitrile using the standard viologen preparation method with a one-step reaction (Ding et al., 2019). Due to the advantage

that no by-products are formed in the reaction procedure, the pure product precipitated in the reaction medium was filtered. $^1\text{H-NMR}$ and FT-IR techniques were used for the chemical characterization of the obtained ALV-Br. According to the $^1\text{H-NMR}$ analysis, 4 different protons attributed to the bipyridyl bridge were observed at 9.38 ppm and 8.33 ppm as doublets, depending on their neighboring to the nitrogen atom. In addition, the protons belonging to the allyl groups attached to the nitrogen atom were observed to be 6.21, 5.52 and 5.40 ppm, respectively. The results obtained from the $^1\text{H-NMR}$ spectrum clearly show that the synthesis of ALV-Br has been carried out successfully (Figure 5).

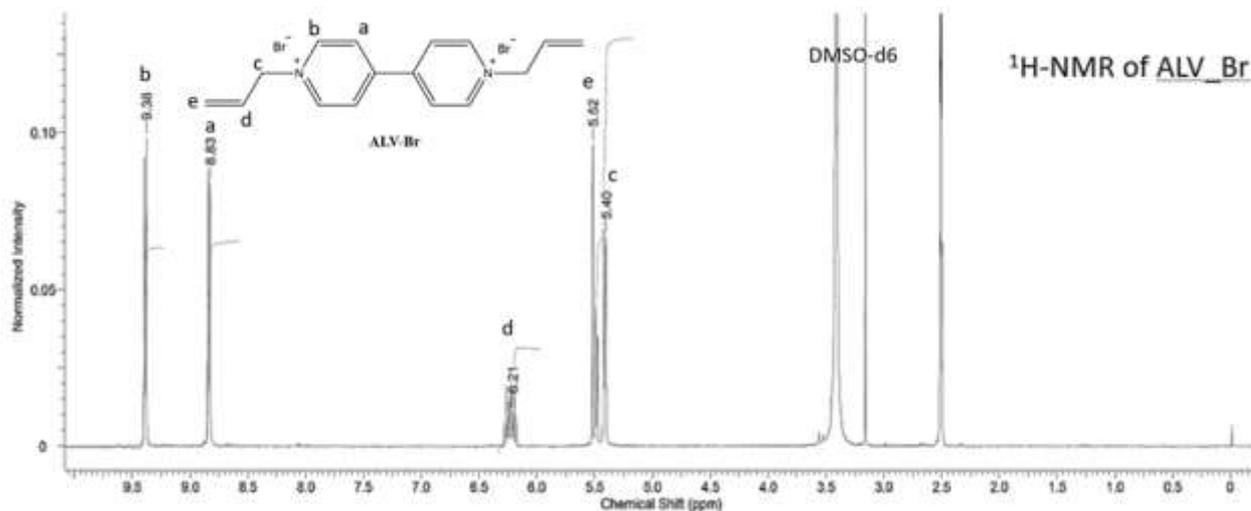


Figure 5. $^1\text{H-NMR}$ spectrum of ALV-Br

FT-IR technique was used to follow the reaction of ALV-Br and ALV-BrX. Looking at the FT-IR spectrum of ALV-Br, the peaks observed at 1622 and 1170 cm^{-1} , unlike the starting compounds 4,4-Bipyridyl and allyl bromide, attributed to the C=N and C-N moieties in the pyridinium salt. When the FT-IR spectrum of ALBrX, which is the crosslinking product of ALV-Br on the film surface using tetrathiol-based crosslinker, is examined, it is seen that the peaks broadened as a result of polymerization on the film surface. In addition, the vibration of the C=O bond in the structure of the crosslinker was clearly observed at 1745 cm^{-1} , while the aliphatic vibrations of the $-\text{CH}_2-$ bridges formed due to the opening of the allyl double bonds via Thiol-en click reaction were clearly observed below 3000 cm^{-1} (Figure 6).

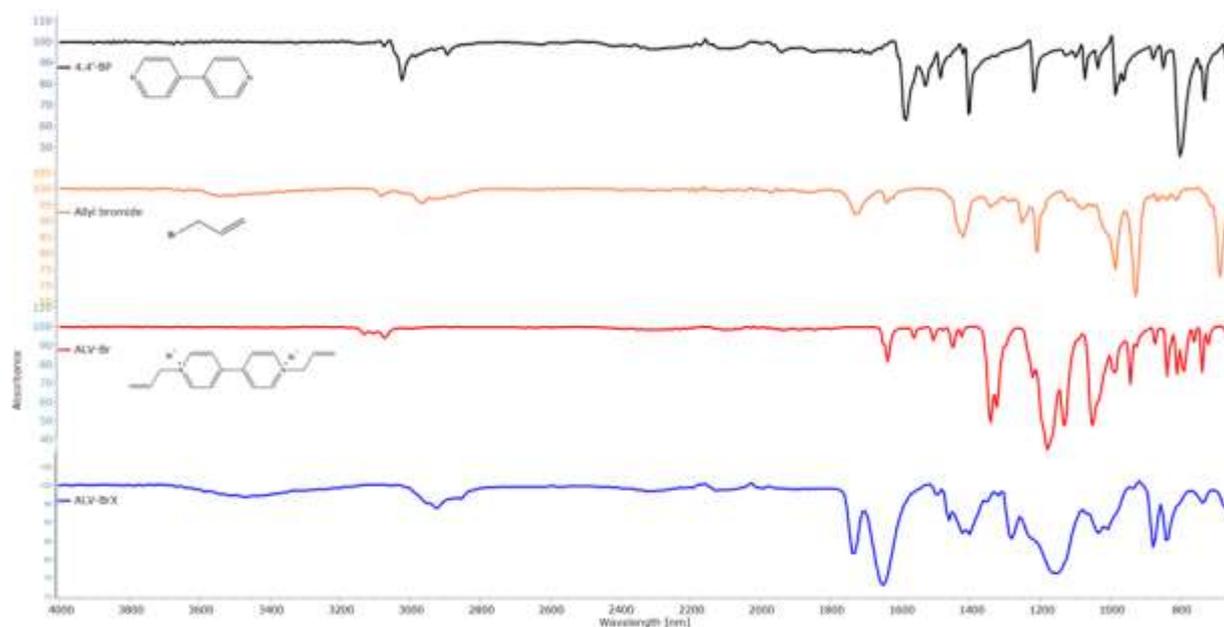


Figure 6. The FT-IR spectra of initial compounds and final products

3.2. Theoretical Calculations

Using the density functional theory method (DFT), the geometrical and structural characteristics of 4,4'-BP, ALV-Br, and ALV-BrX were optimized, and the HOMO-LUMO orbital contributions were calculated using the B3LYP basis set (Table 1). According to these results, the charges concentrated on the pyridine ring at HOMO in the 4,4'-BP structure as the starting compound, are distributed over the entire unit at LUMO. In the ALV-Br structure, while the charges are collected in the centre of the conjugated structure at HOMO, it has been observed that they migrate on the cationic terminal groups formed due to the pyridinium salt structure at LUMO. As a result of the crosslinking, it was observed that the charges were on the electroactive viologen structure at HOMO and concentrated on the tetrathiol-based crosslinker centre at LUMO. Finally, theoretical calculations proved that the structure obtained from the charge distributions at HOMO and LUMO exhibits bipolar behaviour.

Table 1
Molecular orbital diagrams of 4,4'-BP, ALV-Br, ALV-BrX

	LUMO+1	LUMO	HOMO	HOMO-1
4,4'-BP				
ALV-Br				
ALV-BrX				

3.3. Electrochemical and Optical Properties

Cyclic voltammetry (CV) technique was used to examine the electrochemical properties of ALV-Br and ALV-BrX (Figure 7). The reduction of the C=N group at the pyridine centers can be seen as a semi-reversible peak at about -1.75 V on the CV voltammogram of the starting compound, 4,4'-BP. The two-step reversible reduction waves shifted to -0.30 V and -0.70 V, and this shift is the proof that the di-cationic form of the viologen group in the ALV-Br salt structure was successfully obtained (Shah et al., 2019). On the other hand, the two-step reduction of ALV-BrX shifted to the lower potential after the crosslinking process as a result of the network structure formed, and was recorded at -0.20 V and -0.65 V. As a result, the calculated LUMO values for 4,4'-BP, ALV-Br, and ALV-BrX were found to be -2.78 eV, -4.24 eV, and -4.27 eV, respectively. Accordingly, the low LUMO values obtained showed that they could be an ideal acceptor material for OLED, ECD and OPVs (Striepe & Baumgartner, 2017).

The optical behavior of ALV-Br on both solution and thin film surface was investigated using UV-Vis absorption spectrophotometer and the results were compared with cross-linked ALV-BrX polymer thin film (Figure 8). A broad band with a centered at about 270 nm and extending to 310 nm was seen in the UV-Vis measurement of ALV-Br in methanol. Due to the high π - π interaction at the solid state, a 310 nm-centered band with about 40 nm redshift was seen in the absorption spectrum over the thin film of ALV-Br prepared by spray coating. After the crosslinking process the new shoulder band centered at about 350 nm was observed due to the interaction between the tetra-thiol crosslinker and ALV-Br as charged viologen derivative. ALV-BrX thin films can be used in UV protective coating technology because they selectively absorb the entire UV region.

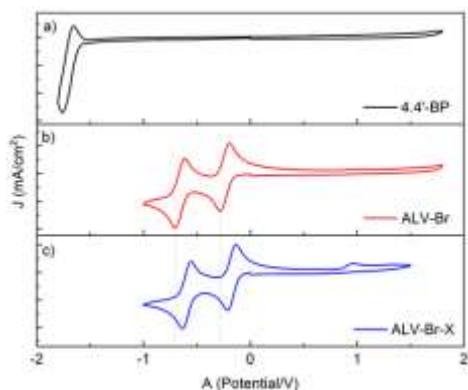


Figure 7. The cyclic voltammograms of ALV salts

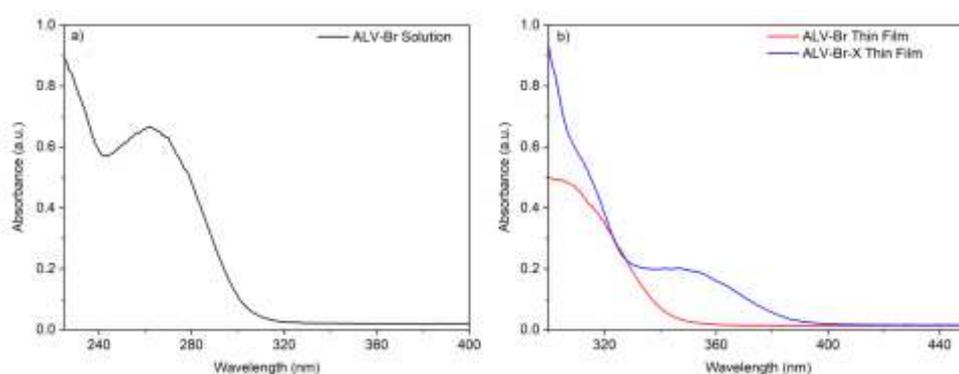


Figure 8. The UV-Vis absorbance measurements of ALV salts in solution (a), and on thin film (b)

3.4. Surface Morphology

When the AFM image of the bare ALV-Br thin film prepared from its solution without using crosslinker is examined, a relatively smooth surface was observed (Figure 9). The smooth surface of the bare film is due to the high interaction between the glass surface and the ALV-Br as charged structure. However, when the AFM image of the ALV-BrX film prepared in the presence of tetra-thiol based crosslinker was examined, it was observed that agglomerations occurred on the film surface and a rougher surface was formed. Accordingly, the RMS value increased from 29.5 nm to 162.2 nm after the cross-linking process. The obtained rough surface as a result of cross-linking will increase the electrochromic performance depending on the high surface area, especially used as catalyst (Altınışık & Koyuncu, 2023).

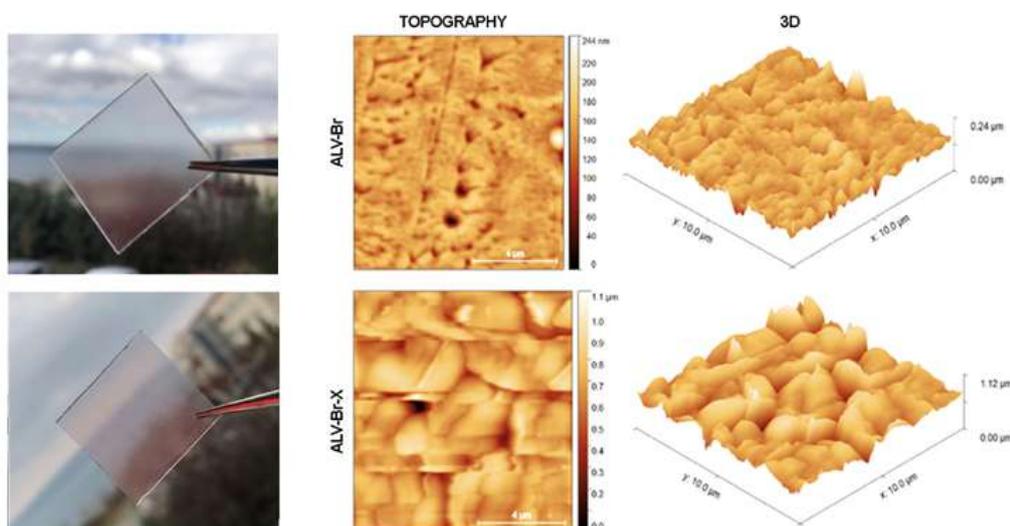


Figure 9. AFM images of ALV-Br and ALV-BrX films

4. Conclusion

In summary, a new viologen derivative with allyl subunit was synthesized and a photopatterning study was performed by direct crosslinking on the film surface with thiol-ene click chemistry. After the cross-linking process, optical and electrochemical properties were investigated both in solution and on the thin film surface. Due to the breakage of the terminal allyl subunit in the ALV-Br, a remarkable red-shift was observed on the thin film absorption spectra. In addition, the theoretical DFT calculations were in agreement with the experimental results, and as a result of geometric optimization, it was determined that the polymer structure showed bipolar behaviour between HOMO and LUMO. The thin film surfaces prepared by crosslinking showed both rough-ness and agglomeration, as determined by AFM measurements. Finally, this method is suitable for fabricating multilayer and patterned optoelectronic devices with the whole solution process for ALV-BrX-based small molecules.

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Author Contributions

Sermet Koyuncu: Conceived and designed the experiments and analysis, supervisor and wrote the paper.

Şölen Ayaşlıgil: Collected data from experiments and analysis and wrote the paper, investigator.

Conflicts of Interest

The authors declare no conflict of interest.

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