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Diclofenac-Derived Organotin(IV) Complexes as Efficient Photostabilizers for Poly(vinyl chloride) Films Under UV Irradiation

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Abstract

This study reports the synthesis and evaluation of diclofenac-derived organotin(IV) complexes as photostabilizing additives for poly(vinyl chloride) (PVC). Diclofenac was selected as a ligand due to its aromatic structure and heteroatom-rich framework, enabling the formation of stable tin-based complexes with potential UV-absorbing and radical-scavenging properties. The synthesized di- and tri-organotin complexes were incorporated into PVC films at 0.5 wt.% and exposed to UV irradiation (365 nm) for up to 300 h to assess their stabilizing efficiency. Photodegradation was monitored by tracking changes in carbonyl, polyene, and hydroxyl indices, as well as weight loss and surface deterioration. Compared with blank PVC and ligand-containing films, the organotin-modified samples exhibited significantly slower growth of degradation indices, reduced mass loss, and improved surface integrity after irradiation. Among the evaluated additives, the tributyltin complex demonstrated the highest photostabilizing performance, showing superior retention of chlorine content and lower surface roughness parameters. Overall, the results indicate that diclofenac-based organotin(IV) complexes are effective photostabilizers for PVC, with the tributyltin derivative emerging as the most promising candidate for enhancing the durability of PVC materials under UV exposure.

Keywords: PVC; diclofenac; organotin; thin films; morphology; photodegradation

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Academic Editor: Aggelos Avramopoulos

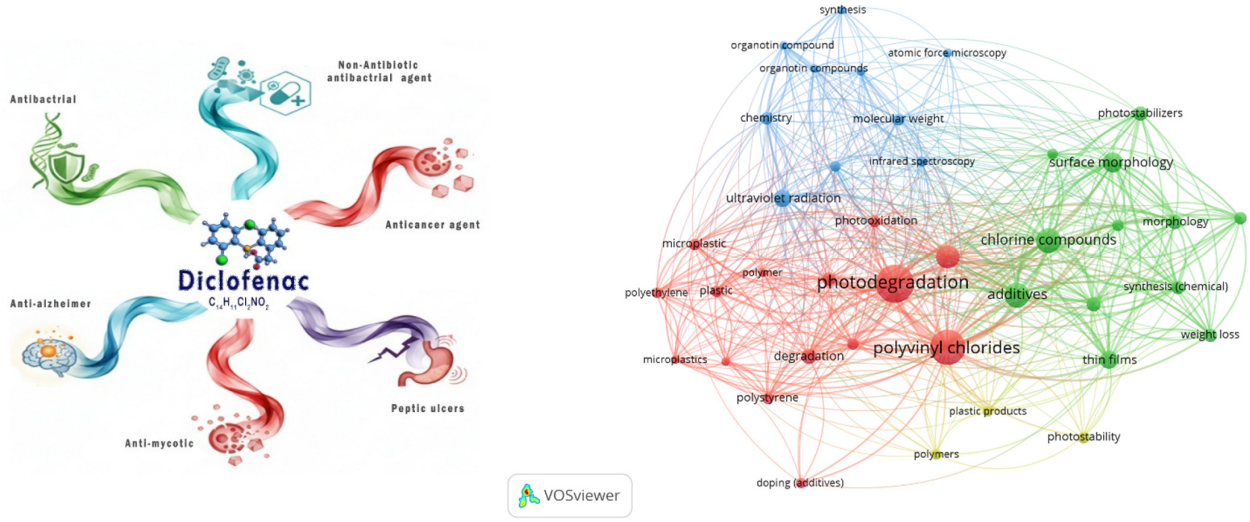
Received: 30 January 2026
Revised: 14 March 2026
Accepted: 25 March 2026
Published: 27 March 2026

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1. Introduction

Diclofenac is reported to have anti-bacterial and anti-mycotic properties [1]. It is a powerful non-antibiotic antibacterial agent that inhibits both Gram-positive and Gram-negative bacteria and exhibits synergism with various antibiotics [2]. While diclofenac has promising prospects as an anticancer agent and in the treatment of other health conditions, the negative effects of diclofenac are a drawback in its use. For example, a recent study

showed that using diclofenac as an adjuvant to curcumin can enhance its anti-Alzheimer benefits in rats [1]. A few studies showed a substantial reduction in the risk of peptic ulcers when proton pump inhibitors and diclofenac were used in combination therapy [3]; Figure 1a shows the health activities of Diclofenac.



(**a**) (**b**)

Figure 1. (**a**) The actions of diclofenac and (**b**) a diagram of publications on PVC degradation and additives.

In recent decades, organometallic chemistry has become an essential discipline in commercial, medical, and academic research [4]. This prominence underscores the essential role of organometallic compounds as intermediates in chemical synthesis and as precursors for many medicinal and technologically important materials [5]. These compounds exhibit structural variety and, in numerous instances, significant chemical reactivity [6]. Moreover, organometallic catalysts have markedly enhanced synthetic efficiency, enabling the synthesis of organic molecules with higher yields and reduced waste [7].

Polyvinyl chloride (PVC) is an economical polymer that may be easily produced in various forms [8]. Rigid PVC is frequently utilized in building and plumbing, whereas flexible PVC is employed in items like clothing and upholstery. Nonetheless, despite these benefits, PVC is linked to environmental and health issues. Disposal is often achieved by incineration, which can generate harmful by-products, or by landfilling as part of municipal solid waste [9,10]. Additives may act as plasticizers, UV absorbents, blowing agents, stabilizers, lubricants, fillers, flame retardants, softeners, colorants, and crosslinking agents. UV stabilizers are capable of reducing the rate of photo-oxidation. The selection of additives is influenced by several aspects, including the intended stability, color, compatibility with volatility, and cost. Moreover, they are required to possess the capacity to absorb or deflect ultraviolet (UV) radiation and convert it into heat or harmless rays at a moderate rate. Recent research has focused on developing plasticized PVC materials with enhanced durability for outdoor use [11]. Plastic formulations typically include several types of additives, such as pigments, plasticizers, flame retardants, and stabilizing agents. To be practically applicable, these additives should be cost-effective, easy to incorporate, and highly efficient at low loading levels while preserving the inherent physical properties of the polymer, particularly its color. Environmental compatibility is also a critical requirement for modern plastic additives [12]. Ideally, these materials should exhibit strong chemical stability, low volatility, and uniform dispersion throughout the polymer matrix. Additives may be introduced into the polymer in various physical forms, including powders, flakes, beads,

and spheres [13,14]. Their function is to mitigate light-induced degradation processes by serving as UV absorbers, energy dissipaters, radical inhibitors, and antioxidant agents [15]. Figure 1b shows a general diagram regarding the publications that were indexed in Scopus when searching for the words "PVC", "photodegradation", and "additives" in the fields "Article title, Abstract, Keywords".

Diclofenac is known to undergo photochemical reactions in solution, including excited-state decarboxylation, cyclization to carbazole derivatives, and the formation of reactive oxygen species through both Type I (radical-mediated) and Type II (singlet oxygen) pathways under aerobic conditions [16]. However, these processes are typically observed in solution systems where molecular mobility and oxygen availability are relatively high. In the present work, diclofenac is coordinated to a Sn(IV) center and dispersed at low concentration within a solid PVC matrix. Coordination to the metal center and restricted mobility within the polymer environment can significantly modify the ligand's photochemical behavior [17]. Therefore, diclofenac–organotin complexes are expected to behave differently from free diclofenac in solution and may instead contribute to the stabilization of PVC during UV irradiation [18].

In our study, we report the synthesis of a series of diclofenac-based tin complexes and present a detailed account of their preparation. Nevertheless, additional investigations are needed to elucidate their structure–activity relationships and to refine their molecular design to improve stabilizing performance. Accordingly, several organotin(IV) complexes synthesized from diclofenac were characterized to evaluate their efficacy in protecting PVC against irradiation-induced degradation. Diclofenac exhibited substantial stability in the solid state. The aromatic framework and significant heteroatom content of the tin complexes indicate their strong potential as efficient stabilizing agents capable of suppressing PVC photodegradation.

2. Materials and Methods

2.1. Chemicals and Devices

Diclofenac sodium, dibutyltin dichloride, tributyltin chloride, and other organotin precursors were purchased from Sigma–Aldrich (Darmstadt, Germany) and used as received with a purity of ≥98%. Solvents such as tetrahydrofuran (THF), methanol, and chloroform were obtained from Merck (Darmstadt, Germany) and used without further purification. The thickness of the films was controlled during the solution casting process and measured using a vernier caliper instrument at several different points across the film surface. The identification of the produced compounds was conducted utilizing multiple spectroscopic techniques. Initial characterization was conducted using Fourier transform infrared (FTIR) spectroscopy with a Shimadzu 8300 FTIR spectrophotometer (Kyoto, Japan). Additional investigation was performed by obtaining ^{1}H and ^{13}C NMR spectra in DMSO-d6, using TMS as the reference standard on a Bruker DRX300 spectrometer (Bruker, Karlsruhe, Germany). Complementary NMR measurements, comprising ^{119}Sn NMR spectra at 107 MHz, were conducted utilizing Varian INOVA (Varian Inc., Palo Alto, CA, USA) and Bruker DRX devices. NMR samples, consisting of 20 mg of the substance dissolved in 2 mL of Dimethyl sulfoxide (DMSO) at room temperature, were prepared and analyzed using 400 MHz ^{1}H and ^{13}C NMR, and 107 MHz ^{119}Sn NMR. The Brunauer–Emmett–Teller (BET) method has been utilized to determine the specific surface area of the solids. Nitrogen adsorption and desorption measurements were performed using a Quantachrome analyzer to evaluate the samples' textural properties. Before analysis, the samples were degassed at 200 °C for 5 h under anhydrous nitrogen. Pore size distributions were calculated according to the Barrett–Joyner–Halenda (BJH) model, while total pore volumes were determined at a relative pressure (P/P^{o}) of 0.98. Surface morphology was examined by field-emission

scanning electron microscopy (FESEM) using a Zeiss device operated at 25 kV. Atomic force microscopy (AFM) imaging was performed with a Veeco system.

2.2. Synthesis of Complexes

The following sections show the preparation methods of the complexes and films. Here, we would like to mention that the ligand was numbered as 1, while the produced complexes were numbered as **2**, **3**, and **4**.

2.2.1. Synthesis of Complexes **2** and **3**

A suitable amount of diclofenac (0.592 g, 2.0 mmol) was reacted with either diphenyltin dichloride (Ph_2SnCl_2; 0.343 g, 1.0 mmol) or dimethyltin dichloride (Me_2SnCl_2; 0.219 g, 1.0 mmol) in boiling methanol (30 mL). The resultant solution was sustained under reflux with constant agitation for 8 h. After cooling to room temperature, the reaction mixture was filtered, and the crude solid was refined by recrystallization from 15 mL of methanol, leading to the formation of the target organotin complexes (complexes **2** and **3**).

2.2.2. Synthesis of Complex **4**

Tributyltin chloride (Bu_3SnCl; 0.325 g, 1.0 mmol) was reacted with diclofenac (0.296 g, 1.0 mmol) in 30 mL of boiling methanol under continuous stirring for 6 h. The reaction mixture was subsequently allowed to cool to ambient temperature and filtered to isolate the crude solid. Purification by recrystallization from methanol (15 mL) yielded the target organotin complex (complex **4**).

2.3. Manufacturing of PVC Films

A total of 5.0 g of PVC was combined with 0.5 wt.% of the complexes and dissolved in 100 mL of tetrahydrofuran under continuous stirring at room temperature for 2 h to achieve homogeneity. The homogenous solution was then applied to glass substrates to create uniform films with an average thickness of 40 µm. The films were subsequently vacuum-dried to remove residual solvent before characterization. Figure 2 shows a diagram for the preparation procedure of the complexes (**2** and **3**) and the preparation of the films (**4**).

2.4. Examination of PVC Photodegradation via the Weight Loss Method

By estimating the polymer's weight loss during irradiation in the presence of stabilizers, the photo-stability of PVC was also investigated. Equation (1) was thus used to compute weight loss [16].

$$\text{Weight loss}(\%) = \frac{W_0 - W_t}{W_0} \times 100 \quad (1)$$

where W_0 represents the PVC weight before irradiation and W_t is the weight following radiation.

2.5. Examination of PVC Photodegradation via FTIR

FTIR spectroscopy was employed to study the photodegradation of the polymer films by tracking the development of carbonyl (C=O) and alkene (C=C) functional groups. The functional group index (I_s) corresponding to these groups was determined using Equation (2) [17].

$$I_s = \frac{A_s}{A_r} \quad (2)$$

Here, A_r is the absorbance's standard peak, and A_s is the one for the functional group.

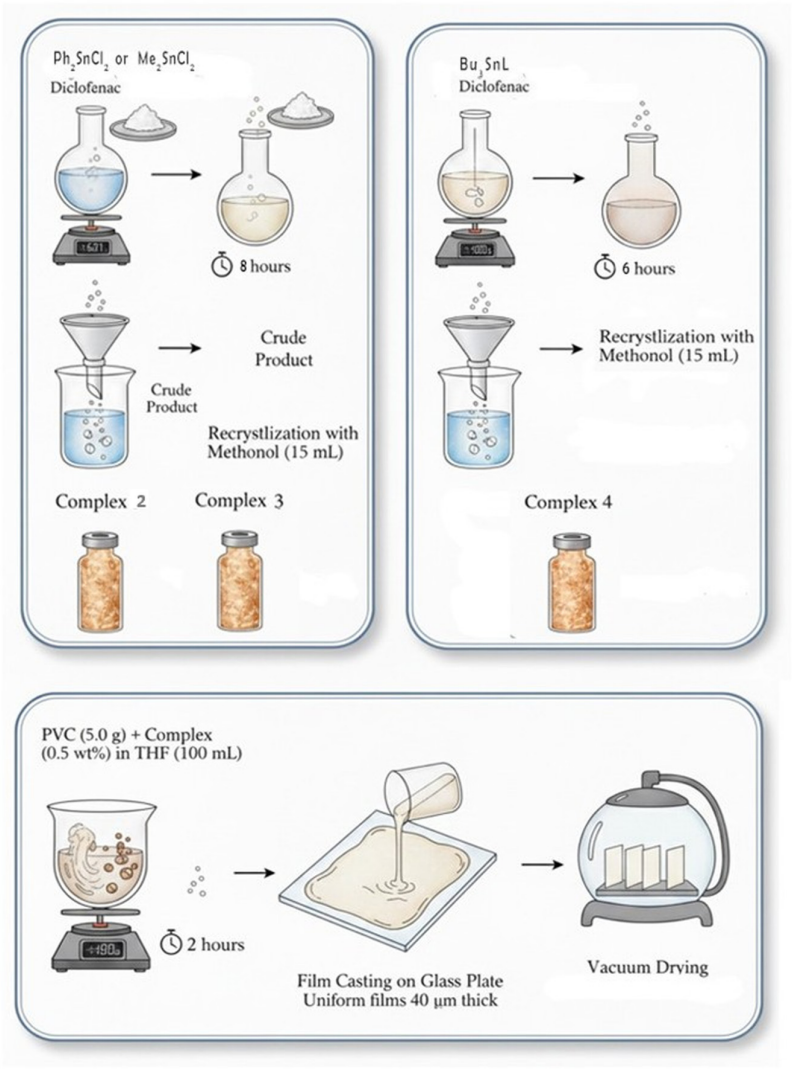


Figure 2. The preparation procedure of the complexes (**2** and **3**) and the preparation of the films (**4**).

3. Results and Discussion

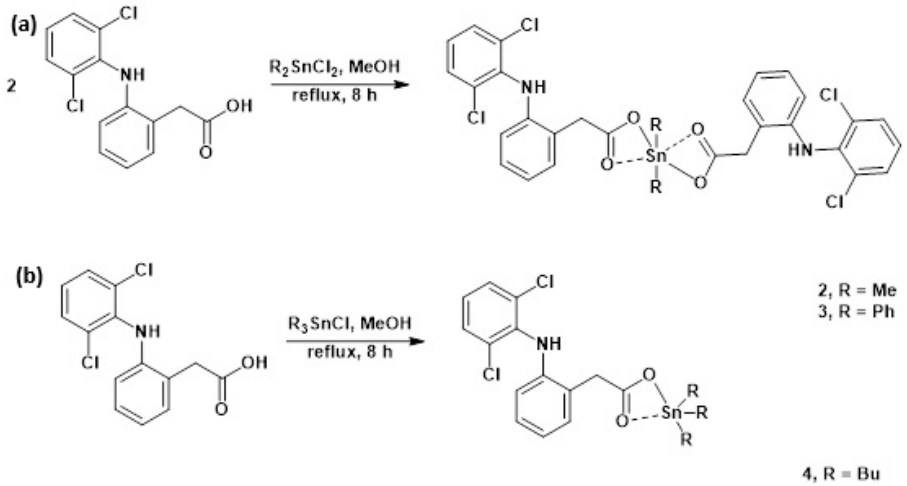
3.1. The Complexes Preparation and Physical Properties

With an off-white color, diclofenac–tin complexes (**2**, **3**, and **4**) were synthesized with favorable yields as illustrated in Scheme 1. Two diorganotin complexes were synthesized by reacting two moles of diclofenac with one mole of diorganotin dichlorides (dimethyltin dichloride and diphenyltin dichloride), while a triorganotin complex was produced by mixing one mole of diclofenac with one mole of tributyltin chloride. In each instance, the diclofenac molecules substituted the chlorine atoms in the tin precursors. The comprehensive synthesis pathways for organotin(IV) complexes **2**–**4** are delineated in Scheme 1.

The ligand and the obtained complexes were tested using FTIR, ^{1}H NMR, ^{13}C NMR, and ^{119}Sn NMR spectroscopy. Selected physical properties for the organotin complexes **2**–**4** are listed in Table 1.

Table 1. The physical properties of organotin complexes.

Complex	R	Color	Yield (%)	M.P. (°C)
1	L	White	-	286
2	Me	White	78	173
3	Ph	White	80	140
4	Bu	White	72	250



Scheme 1. Synthesis of organotin(IV) complexes: (**a**) for **2** and **3** and (**b**) for **4**.

3.2. Characterization of Synthesized Complexes by FTIR

The FTIR spectra of pure diclofenac ligand (L) and synthesized organotin(IV) complexes (Me_2SnL_2, Ph_2SnL_2, and Bu_3SnL) demonstrate clear and reasonable changes that indicate coordination of L to Sn by carboxylate oxygen atoms with stability of the organotin alkyl/aryl groups. The ligand shows a broad NH and OH stretching band at 3386 cm^{-1}, aromatic and aliphatic C–H stretches at 3078 cm^{-1} and 2972 cm^{-1}, and strong carboxylate absorptions at 1573 cm^{-1} and 1398 cm^{-1} that belong to asym and sym COO^{-}, respectively. After complexation, the NH band became sharper with slight shifts 3352–3485 cm^{-1}, indicating that the amino group is not directly involved in bonding [19].

On the other hand, remarkable changes are observed in the carboxylate region, where the $\Delta\nu$ ($\nu_{asym} - \nu_{sym}$) values for the complexes (ranging from 152 to 199 cm^{-1}) differ from those of the free ligand. This confirms that coordination happens through the oxygen atoms of the carboxylate group. The synthesized complex Me_2SnL_2 shows a strong band at 1739 cm^{-1}, which may indicate partial retention of a free carbonyl group or mixed coordination modes. New absorptions in the 667–617 cm^{-1} and 520–451 cm^{-1} regions are assigned to ν(Sn–C) and ν(Sn–O) vibrations, confirming the formation of Sn–O bonds and retention of Sn–C linkages from the organotin precursors. The C–O stretching band of the ligand (1284 cm^{-1}) shifts to higher frequencies (1296–1305 cm^{-1}) upon coordination, while the C–Cl and aromatic C–H bands remain largely unchanged. This suggests that the aromatic system and chloro substituents are not affected. The FTIR spectra of the other complexes changed correspondingly; this supports the proposed coordination of diclofenac to the tin center via carboxylate oxygen atoms, forming stable organotin(IV) complexes (Ph_2SnL_2 and Bu_3SnL) with varying carboxylate binding modes depending on the organic substituents attached to the tin atom. Table 2 summarizes the FTIR data of ligand and synthesized complexes (Me_2SnL_2, Ph_2SnL_2, and Bu_3SnL). All FTIR spectra are provided in the Supplementary Materials [20].

Table 2. The FTIR data for diclofenac–tin complexes.

Compounds	Wave Number (cm^{-1})									
	NH	C–H Ar	C–H Alph	C=O	C=C	C–O	C–C	C–Cl	Sn–C	Sn–O
L	3386	3078	2972	1573	1452	1398	1284	746	-	-
Me_2SnL_2	3352	3082	2952	1739	1583	1296	1147	779	659	478
Ph_2SnL_2	3433	3068	2964	1575	1542	1390	1305	771	617	451
Bu_3SnL	3485	2956	2856	1581	1454	1382	1301	771	667	520

3.3. Characterization of Synthesized Complexes by ^{1}H NMR

The ^{1}H NMR technique was also utilized to confirm the chemical structure of the synthesized complexes. Thus, the spectra of ligand (L) and synthesized organotin(IV) complexes further confirm the successful coordination of diclofenac to the tin center. For pure ligand, the characteristic singlet at δ 10.32 ppm corresponds to the NH proton, while aromatic protons appear between δ 7.50–6.24 ppm and the aliphatic CH_2 group at δ 3.50 ppm. While after forming the complexes, the NH signals broaden and shift slightly downfield (δ 8.28–11.48 ppm), which indicates the involvement of the carboxylate group in coordination and changes in the electronic environment around the amine. The aromatic region (δ 7.55–6.25 ppm) becomes more complex due to the increased number of aromatic protons from both the ligand and the organotin substituents, which is particularly evident in Ph_2SnL_2, where the phenyl protons of the tin moiety overlap with the ligand signals. Hence, the aliphatic CH_2 group of the ligand observed at δ 3.50 ppm as a multiplet peak in the range δ 3.87–3.18 ppm in all complexes. This is due to the coordination of the ligand to Sn, which induced deshielding. Additional signals at δ 0.86–0.66 ppm in Me_2SnL_2 and δ 0.90–0.50 ppm in Bu_3SnL are attributed to the methyl and butyl protons attached to the tin atom, confirming the presence of the organotin substituents. The existence of the NH proton signal in all complexes confirms that the nitrogen does not participate directly in bonding, as this result is consistent with the FTIR findings. Table 3 presents the ^{1}H NMR data of the ligand and the prepared complexes (Me_2SnL_2, Ph_2SnL_2, and Bu_3SnL). All ^{1}H NMR spectra are provided in the Supporting File in Figure S2.

Table 3. ^{1}H-NMR spectral data for ligand and tin complexes.

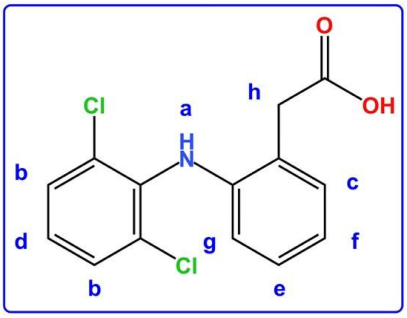
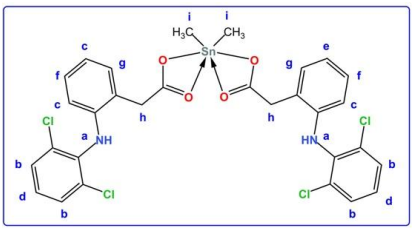
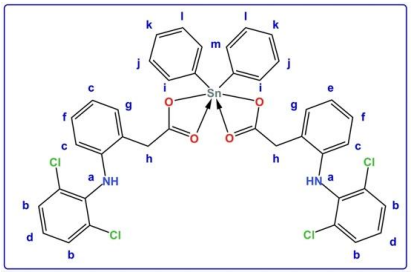
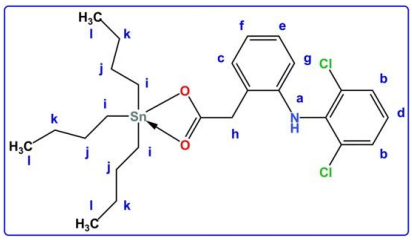
Compound	^{1}H-NMR (400 MHz: DMSO-d_6, δ, ppm)
	The ^{1}H NMR spectrum (DMSO-d_6) exhibited a singlet at δ 10.32 ppm attributed to the NH proton. The aromatic region showed signals at δ 7.50 ppm (s, 2H) corresponding to protons adjacent to the chloro substituent, while multiplet signals appeared at δ 7.10–6.73 ppm (4H, Ar–H) and a singlet at δ 6.24 ppm (1H, Ar–H). In addition, a singlet at δ 3.50 ppm (2H) was assigned to the aliphatic CH_2 group.
	The ^{1}H NMR spectrum showed a broad signal at δ 8.28 ppm corresponding to two N–H protons. The aromatic region exhibited a multiplet at δ 7.53 ppm (4H) assigned to the aromatic protons adjacent to the chloro substituent, while additional multiplet signals appeared in the range δ 7.24–6.82 ppm (8H) attributed to the remaining aromatic protons (Ar–H). A singlet at δ 6.26 ppm (2H) was also observed for aromatic protons. Furthermore, the aliphatic CH_2 groups appeared as a multiplet in the region δ 3.87–3.26 ppm (4H), whereas a broad multiplet at δ 0.86–0.66 ppm (6H) was assigned to the two CH_3 groups.
	The ^{1}H NMR spectrum showed a broad signal at δ 7.85 ppm corresponding to two N–H protons. The aromatic region exhibited multiplet signals in the range δ 7.55–6.84 ppm (12H) attributed to the aromatic protons of the ligand overlapping with ten protons from the two phenyl groups. A singlet at δ 6.25 ppm (2H) was assigned to aromatic protons of the ligand, while the aliphatic CH_2 groups appeared as a multiplet in the region δ 3.78–3.18 ppm (4H).

Table 3. *Cont.*

Compound	^{1}H-NMR (400 MHz: DMSO-d_6, δ, ppm)
	The ^{1}H NMR spectrum showed a broad signal at δ 11.48 ppm corresponding to one N–H proton. The aromatic region displayed a singlet at δ 8.05 ppm (2H) assigned to the aromatic protons adjacent to the chloro substituent, while multiplet signals appeared in the range δ 7.34–7.11 ppm (4H) attributed to the remaining aromatic protons (Ar–H). A broad signal at δ 5.03 ppm (1H) was also observed for an aromatic proton. The aliphatic CH_2 group appeared as a singlet at δ 3.47 ppm (2H). Additionally, multiplet signals in the region δ 3.10–2.06 ppm (12H) were assigned to six overlapping CH_2 groups of the butyl chains, while another multiplet at δ 1.25 ppm (6H) corresponded to three CH_2 groups. Finally, multiplet signals in the range δ 0.90–0.50 ppm (9H) were attributed to three terminal CH_3 groups of the aliphatic butyl substituents.

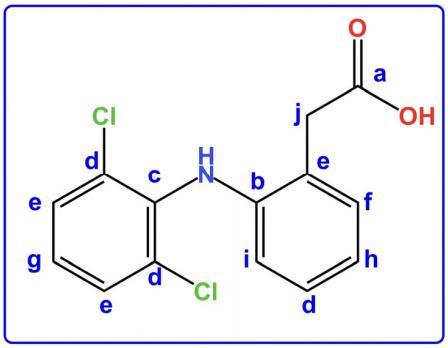
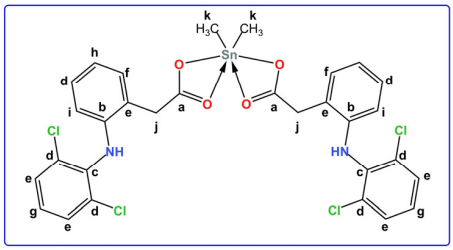
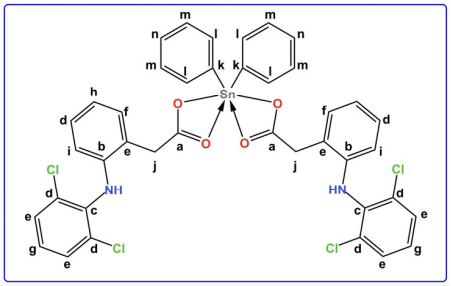
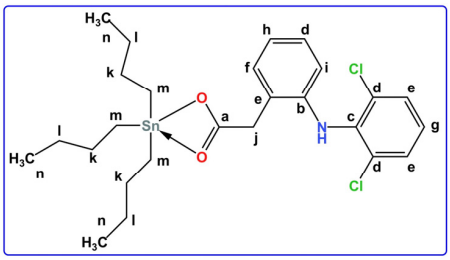
3.4. Characterization of Synthesized Complexes by ^{13}C NMR

The ^{13}C NMR spectra of ligand and synthesized tin complexes (Me_2SnL_2, Ph_2SnL_2, and Bu_3SnL) demonstrated the chemical structure of the synthesized materials. This gives further confirmation of complex formation and coordination through the carboxylate group. In the spectrum of the free ligand, the carbonyl carbon of the carboxylic group appears at δ 175.51 ppm, while the aromatic carbons resonate between δ 143.32–115.46 ppm, and the aliphatic CH_2 carbons appear at δ 44.57 and 39.45 ppm. Upon coordination to tin, the carbonyl signal shifts slightly upfield to δ 171.85–175.17 ppm in the complexes, reflecting a change in electron density around the carboxylate carbon due to coordination with the tin center. The aromatic carbons show minor chemical shift variations, ranging from 142 ppm to 115 ppm. This is compared with the free ligand, indicating that the aromatic ring remains largely unaffected by coordination.

The aliphatic CH_2 carbons experience downfield shifts (δ 36.94–51.91 ppm), consistent with their proximity to the coordinated carboxylate group. In Ph_2SnL_2, the number of peaks resonating in the aromatic region between 129.13 ppm and 127.71 ppm arises from the phenyl groups attached to the tin atom. Thus, in Bu_3SnL, new signals at the aliphatic region appear between 27.70 ppm and 13.67 ppm and are assigned to the methylene and methyl carbons of the butyl substituents. The absence of any significant new signals or major splitting patterns confirms the integration of the ligand framework upon structural coordination. The observed carbonyl shift, along with the appearance of organotin substituent resonances, is clear evidence of the formation of organotin(IV) complexes in which the diclofenac ligand coordinates to the tin atom through the carboxylate oxygen atoms. Table 4 shows the ^{13}C-NMR spectral data for ligand and metal complexes, and Figure S3 shows the spectra.

^{119}Sn NMR spectroscopy was utilized to characterize the synthesized organotin (IV) complexes and to gain insight into the coordination environment of the tin atoms. As shown in the corresponding figures, distinct resonance signals were observed for Ph_2SnL_2 (−508.58 ppm), Bu_3SnL (−546.78 ppm), and Me_2SnL_2 (−574.03 ppm). The pronounced differences in these chemical shifts highlight the strong dependence of ^{119}Sn NMR signals on the nature of the bonding and the coordination environment surrounding the tin centers. The ^{119}Sn NMR spectra of Me_2SnL_2, Ph_2SnL_2, and Bu_3SnL are shown in Figure S4a, b and c, respectively.

Table 4. ^{13}C-NMR spectral data for ligand and metal complexes.

Compound	^{13}C-NMR (400 MHz: DMSO-d$_6$, δ, ppm)
	175.51, 143.32, 138.15, 130.0, 128.89, 125.6, 123.7, 119.73, 115.46, 44.57, 39.45.
	171.85, 142.78, 136.99, 130.93, 127.71, 126.71, 123.00, 120.53, 115.69, 51.91, 39.71, 36.94.
	173.53, 142.09, 136.98, 130.69,129.13, 128.28, 127.71, 125.94, 124.30, 122.99, 120.69, 115.94, 51.90, 38.28.
	175.17, 143.00, 137.72, 130.27, 129.06, 127.36, 126.22, 124.34, 120.31, 115.8, 42.57, 27.70, 26.50, 23.77, 21.27, 18.78, 13.67.

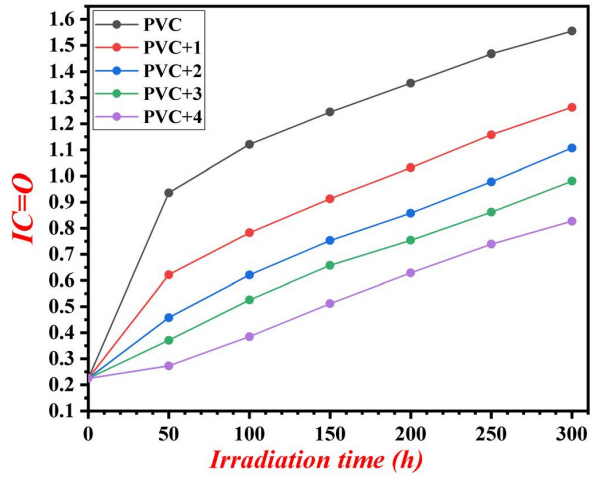
3.5. Monitoring the PVC Films Photodegradation by FTIR Spectroscopy

PVC films, measuring 40 µm in thickness, were subjected to UV radiation at a peak wavelength of 365 nm and a light intensity of 6.43 × 10^{-9} ein·dm^{-3}·s^{-1} for durations up to 300 h. The alterations in the chemical structure of the films were examined via FTIR spectroscopy within the range of 400–4000 cm^{-1}. Photostability was assessed by comparing the relative intensities of the polyene (1602 cm^{-1}), carbonyl (1722 cm^{-1}), and hydroxyl (3500 cm^{-1}) bands with that of a reference peak at 1328 cm^{-1} across varying irradiation durations. Figure S1a depicts the FTIR spectra of the unmodified PVC film prior to and subsequent to 300 h of UV exposure, and Figure S1b–e are the FTIR spectra of the ligand, Me_2SnL_2, Ph_2SnL_2, and Bu_3SnL, respectively.

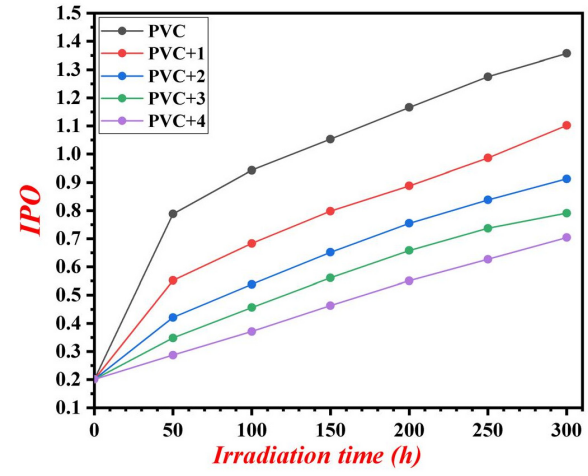
3.6. Carbonyl, Polyene, and Hydroxy Functional Groups Indices

The carbonyl ($I_{C=O}$), polyene (I_{PO}), and hydroxyl (I_{OH}) functional group indices were determined and presented as a function of UV exposure time in Figure 3a–c. In the figures,

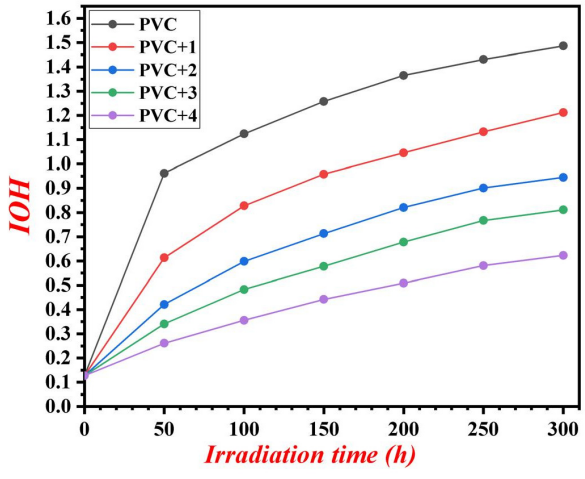
PVC represents the plain film, PVC+1 represents the film with the ligand, and PVC+2, +3, and +4 are the films filled with Me_2SnL_2, Ph_2SnL_2, and Bu3SnL, respectively. PVC films incorporating diclofenac–tin complexes **2–4**, exhibited interestingly lower index values compared with the untreated PVC film. This behavior demonstrates the enhanced photostabilizing effect of diclofenac–tin complexes, among which complex 4 showed the highest stabilizing efficiency.



(**a**)



(**b**)



(**c**)

Figure 3. Effect of irradiation of PVC films on (**a**) $I_{C=O}$, (**b**) I_{PO}, and (**c**) I_{OH}.

3.7. Monitoring the Photodegradation of PVC Films by Weight Loss

The elimination of hydrogen chloride (HCl) via dehydrochlorination constitutes a principal process of PVC photodegradation and correlates with a decrease in polymer mass [21]. The extent of photodegradation can be evaluated by measuring the % weight loss of PVC after UV exposure. The effect of irradiation time on the percentage weight loss of PVC films is shown in Figure 4. Clearly, the weight loss in PVC was lower in the presence of diclofenac tin complexes **2**–**4** compared to the blank PVC film. Complex **4** was the most efficient additive since it could act as an effective radical scavenger. During irradiation of PVC films containing diclofenac tin complexes **2**–**4**, not only was the weight loss reduced, but the discoloration was also less.

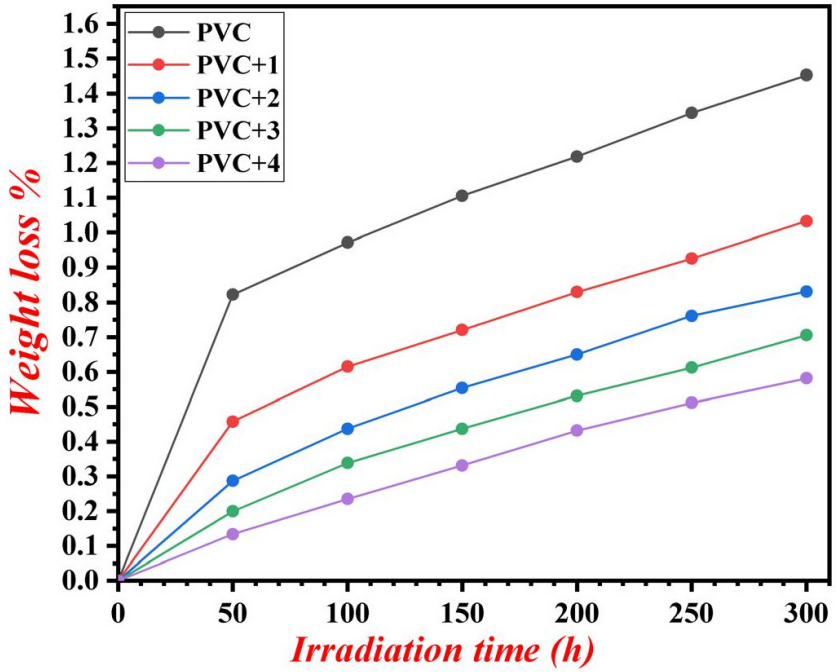


Figure 4. Impact of UV irradiation on the weight loss (%) of PVC films.

3.8. Film Examination via Field Emission Scanning Electron Microscopy

FESEM is commonly applied to investigate morphology and pore structures in materials and films [22]; it provides valuable information on particle size, surface variation, distortion, and homogeneity [23]. The irradiated PVC films exhibit cracks, cavities, protrusions, blemishes, and formlessness, which yield uneven surfaces. These alterations primarily arise from dehydrochlorination, chain fragmentation, and cross-linking [24]. Nevertheless, the presence of UV absorbers restrained surface impairment in polymers relative to the untreated polymers, as illustrated in Figure 5a–d. The PVC blends modified with diclofenac–tin complexes exhibited markedly reduced surface damage, with minimal degradation observed in the formulation containing additive 4.

3.9. The EDX Spectroscopy of PVC Films

Uniform and transparent PVC films were obtained by blending PVC with 0.5 wt.% of the selected diclofenac–tin complexes. The elemental composition of the resulting PVC blends was examined using energy-dispersive X-ray (EDX) spectroscopy [25,26]. The EDX spectra of the UV-irradiated films were dominated by chlorine signals originating from the PVC matrix. At the same time, less intense peaks corresponding to nitrogen and oxygen from diclofenac and tin from the organotin additives were also detected. These observations are consistent with reports in the literature on PVC formulations containing tin-based and similar stabilizing additives [25].

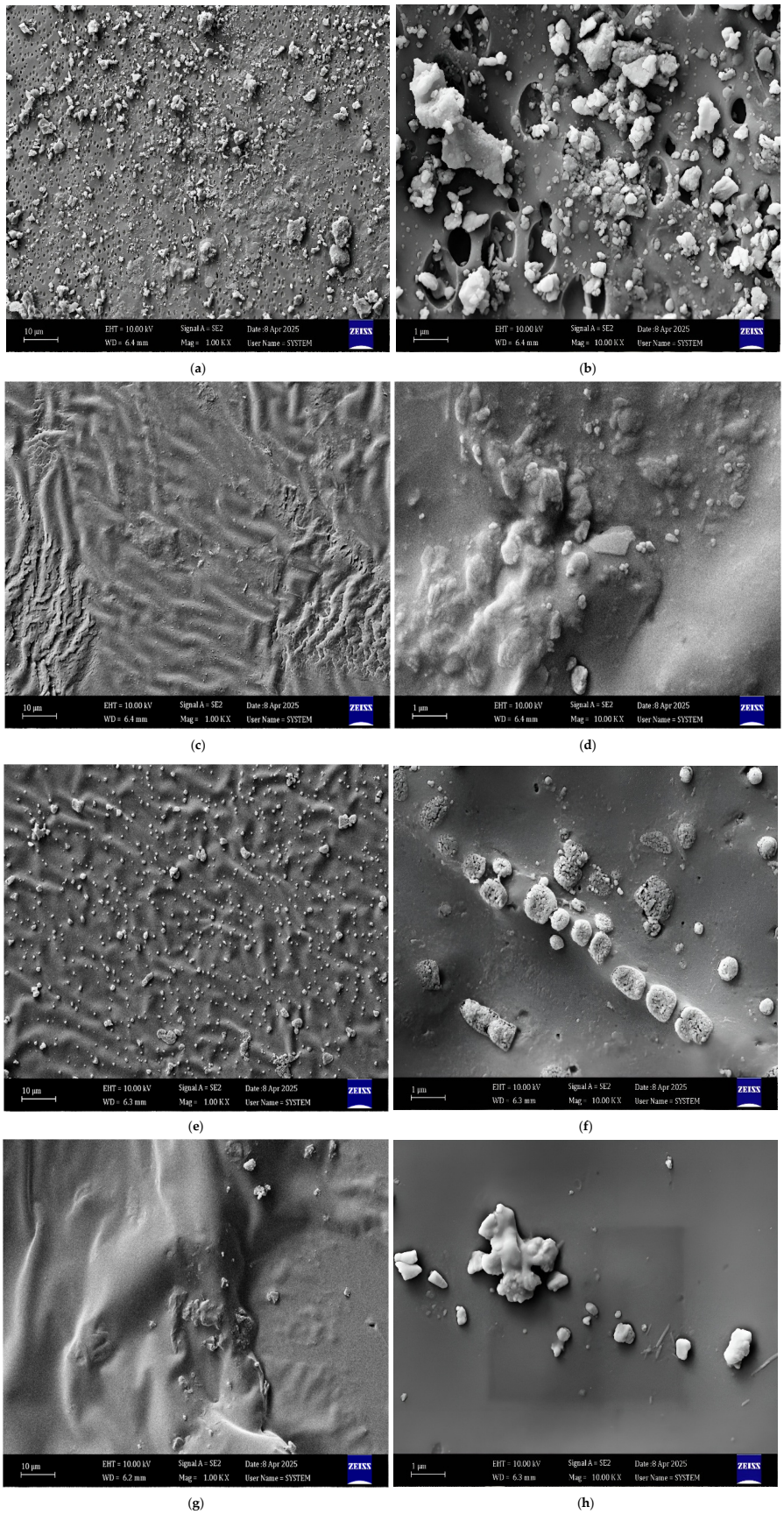
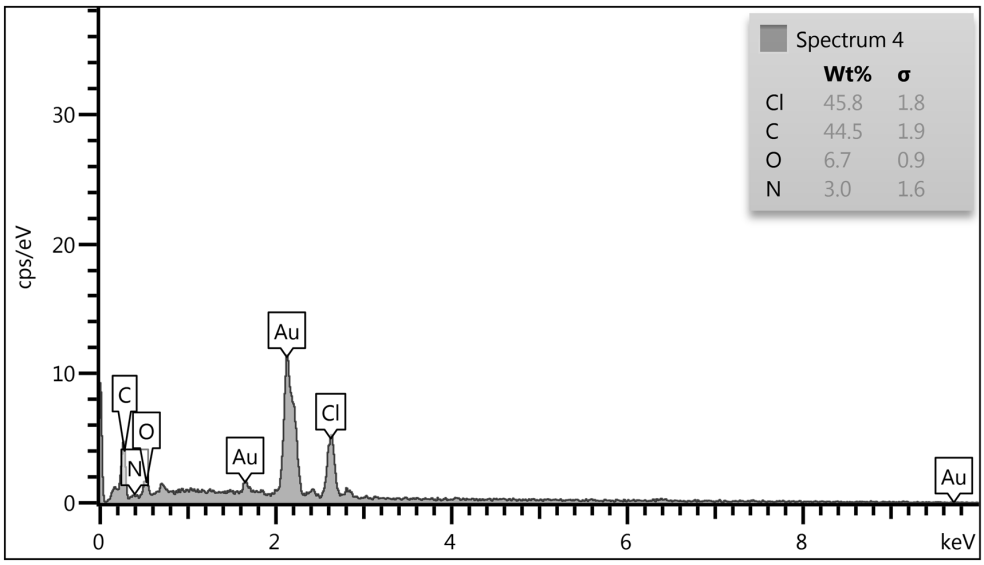
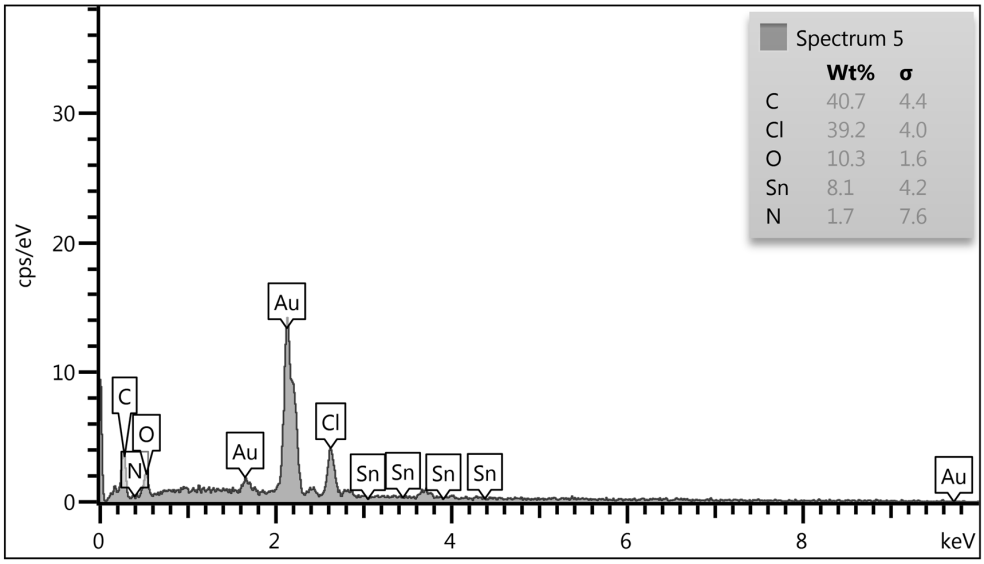


Figure 5. FESEM images of PVC films with the ligand (diclofenac) at (**a**) 1 µm and (**b**) 10 µm, with complex **2** at (**c**) 1 µm and (**d**) 10 µm, with complex **3** at (**e**) 1 µm and (**f**) 10 µm, and with complex **4** at (**g**) 1 µm and (**h**) 10 µm.

Figure 6a–d show EDX elemental mapping of the PVC films filled with the ligand, ligand-complex **2**, ligand-complex **3**, and ligand-complex **4**, respectively. The test verifies the homogeneous distribution and excellent compatibility of the metal complexes inside the PVC matrix. The constituent parts of the complexes, specifically Sn, N, and O, were uniformly distributed throughout the polymer in comparable relative quantities. UV irradiation resulted in a reduction of chlorine content due to the release of volatile species, including HCl. Conversely, PVC films containing diclofenac–tin complexes exhibited noticeably less chlorine loss than untreated PVC films. This behavior validates the efficacy of additives 2–4 in inhibiting PVC photodecomposition, with the film incorporating compound **4** demonstrating the highest residual chlorine level post-irradiation.

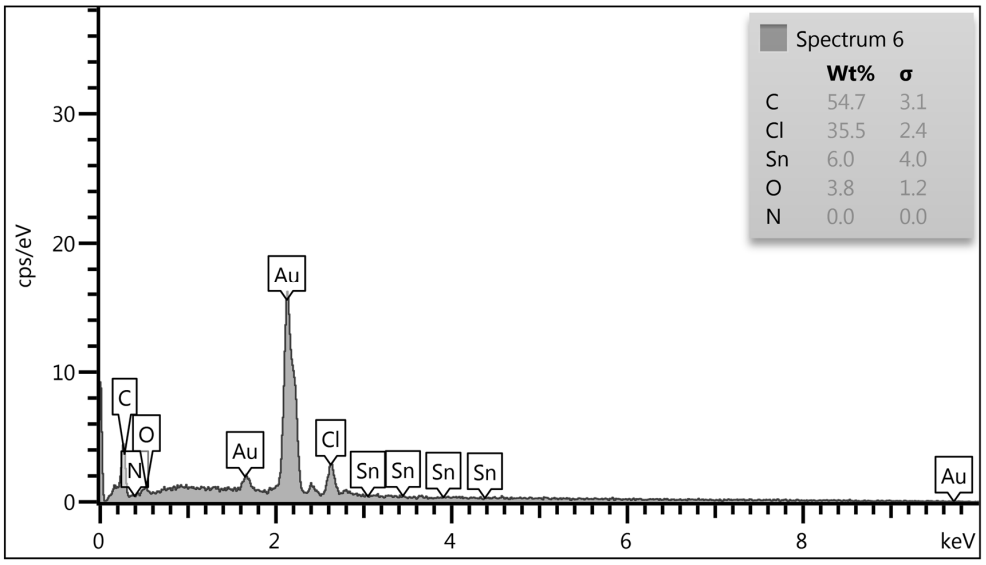


(**a**)

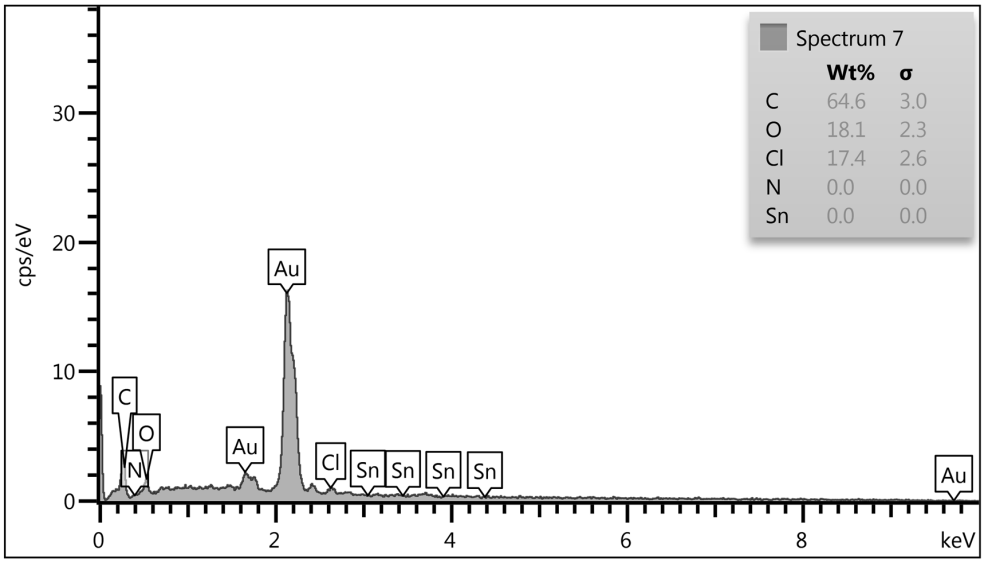


(**b**)

Figure 6. *Cont.*



(**c**)



(**d**)

Figure 6. EDX spectra of PVC films: (**a**) +ligand only, (**b**) +complex **2**, (**c**) +complex **3**, and (**d**) +complex **4**.

3.10. Transmission Electron Microscopy Examination

Prior microscopic images of PVC films after irradiation revealed noticeable deformation when compared to the unexposed film. The irradiated polymer films contained extensive cracks, grooves, and darkened regions. These dark features are associated with HCl evolution resulting from the photodecomposition of PVC [27]. To gain further insight into the irradiation effects, TEM was used to examine the thin-film microstructure at high resolution [28]. The images obtained confirmed significant structural damage resulting from UV exposure. Figure 7a–d illustrate the presence of holes, loops, and segregated regions in the irradiated PVC films, indicating severe photoinduced degradation.

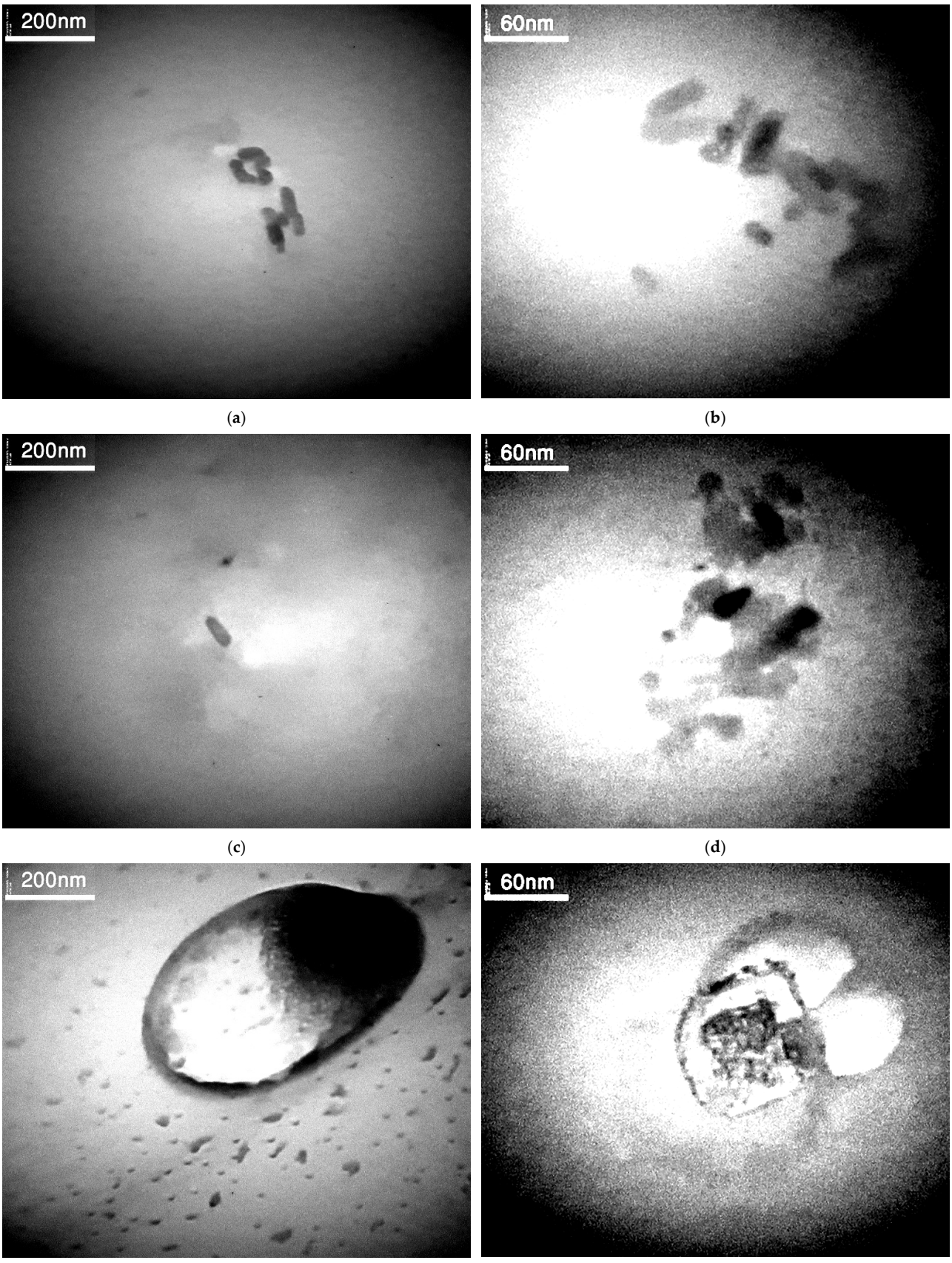
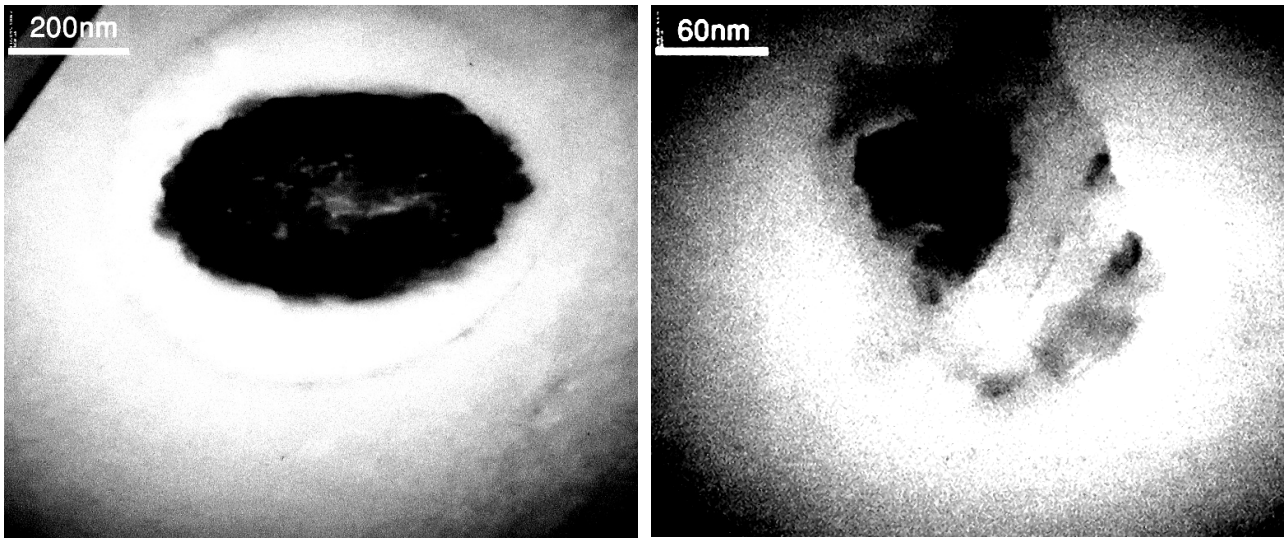


Figure 7. *Cont.*

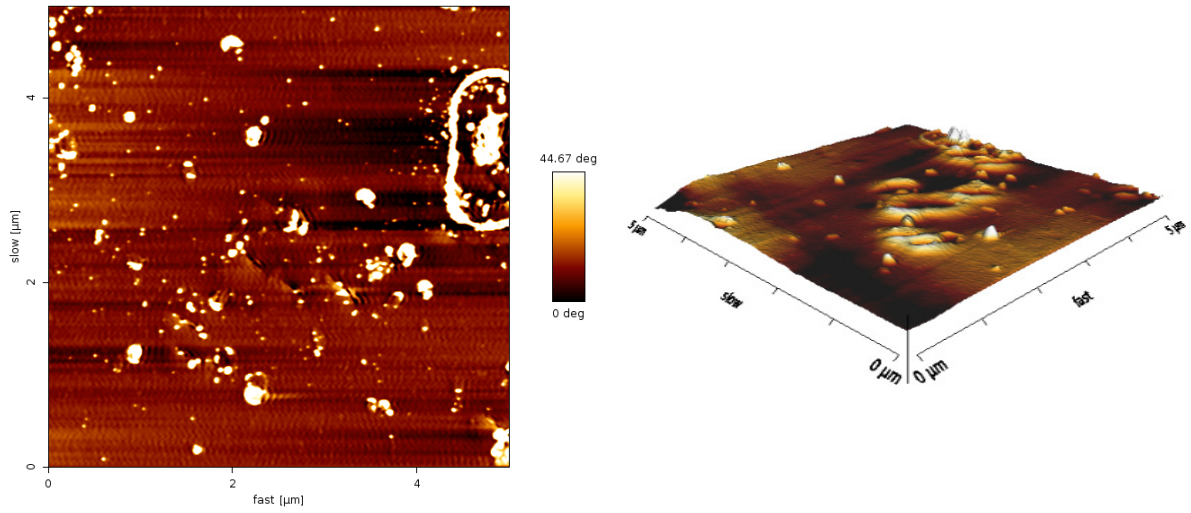


(**g**) (**h**)

Figure 7. FESEM image for PVC film + 1 at (**a**) 200 nm and (**b**) 60 nm, +2 at (**c**) 200 nm and (**d**) 60 nm, +3 at (**e**) 200 nm and (**f**) 60 nm, and + 4 at (**g**) 200 nm and (**h**) 60 nm.

3.11. Atomic Force Microscopy Examination

Figure 8a–d depict the surface morphology of PVC sheets post-irradiation, with the emphasis on considerable roughness. The uncoated PVC film exhibited significant surface imperfections, but the addition of diclofenac–tin complexes **2**–**4** substantially decreased surface roughness. The recorded roughness factors (R_q) were 104.6 for the blank film and 90.3, 77.2, and 51.4 for films incorporating complexes **2**, **3**, and **4**, respectively. These values signify enhanced surface stability with the additions.



(**a**) (**b**)

Figure 8. *Cont.*

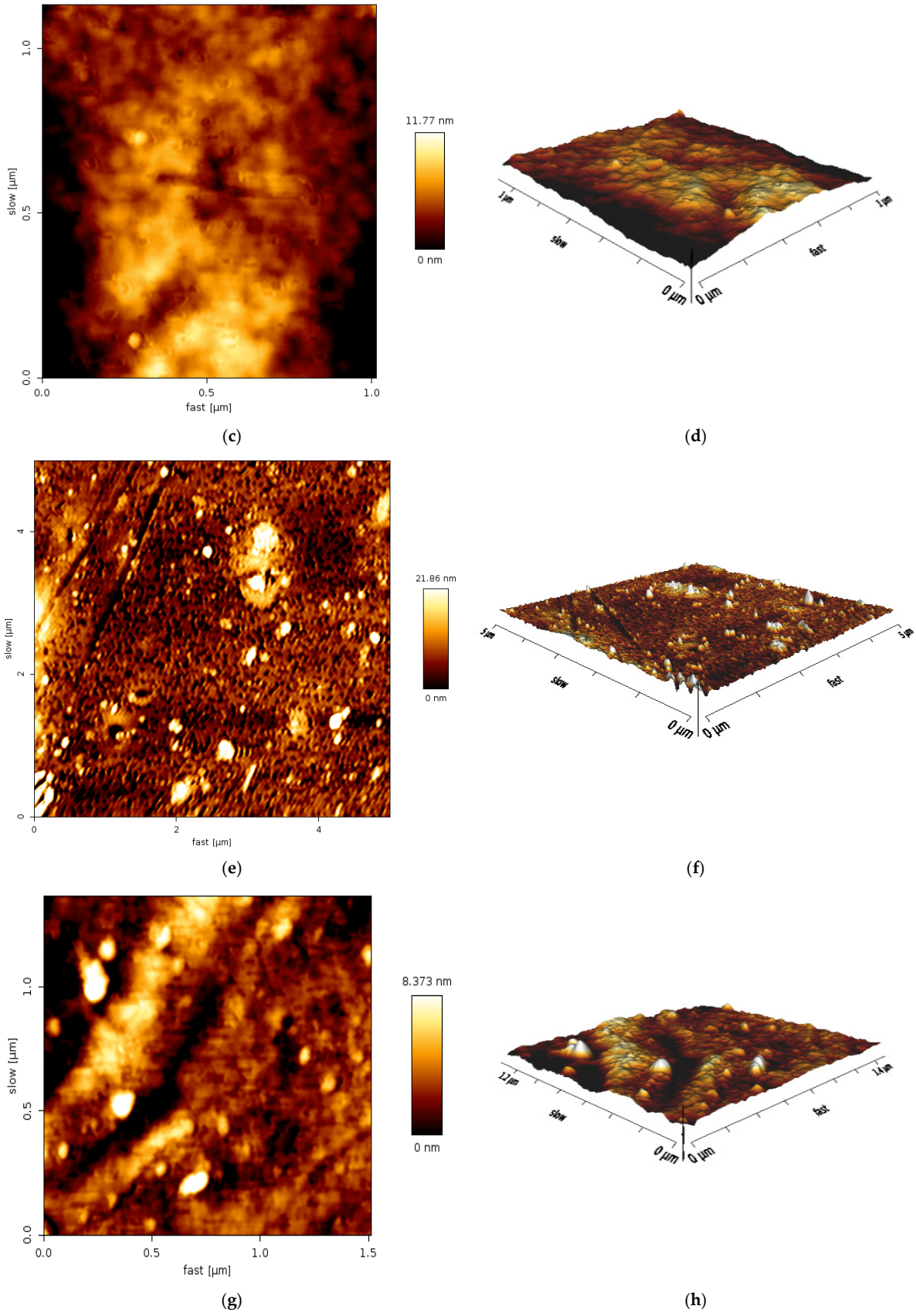


Figure 8. 2D and 3D AFM images of PVC films, +1 (**a**,**b**), +2 (**c**,**d**), +3 (**e**,**f**), and +4 (**g**,**h**).

3.12. Photostabilization Mechanisms

The improved photostabilizing performance of diclofenac–organotin(IV) complexes can be attributed to several contributing factors. The diclofenac ligand contains aromatic rings capable of absorbing ultraviolet radiation and dissipating the absorbed energy, which may reduce direct photolytic damage to PVC chains. In addition, organotin compounds are known to interact with hydrogen chloride released during PVC dehydrochlorination, thereby slowing the autocatalytic degradation process [16,17]. Organotin complexes may also participate in radical scavenging and hydroperoxide decomposition reactions that reduce oxidative degradation. The combined effects of UV absorption, possible HCl interaction, and radical suppression likely contribute to the improved stability of PVC films containing these complexes [26].

Di- and tri-organotin(IV) complexes effectively serve as photostabilizers for PVC films under UV exposure. Their stabilization mechanisms include scavenging HCl due to the strong Lewis acidity of the tin center (Figure 9a) and coordination of carboxylate oxygen atoms with tin(IV), which can substitute for chlorine atoms in the polymer backbone. As secondary stabilizers, these complexes contribute to the prolonged photostability of PVC [28]. Additionally, the tin complexes can act as peroxide-decomposing agents to prevent PVC photodegradation. Photo-oxidation of PVC produces radicals that interact with oxygen, leading to the formation of hydroperoxides (POOH) [29]. These peroxides can subsequently be decomposed by tin complexes, as shown in Figure 9b.

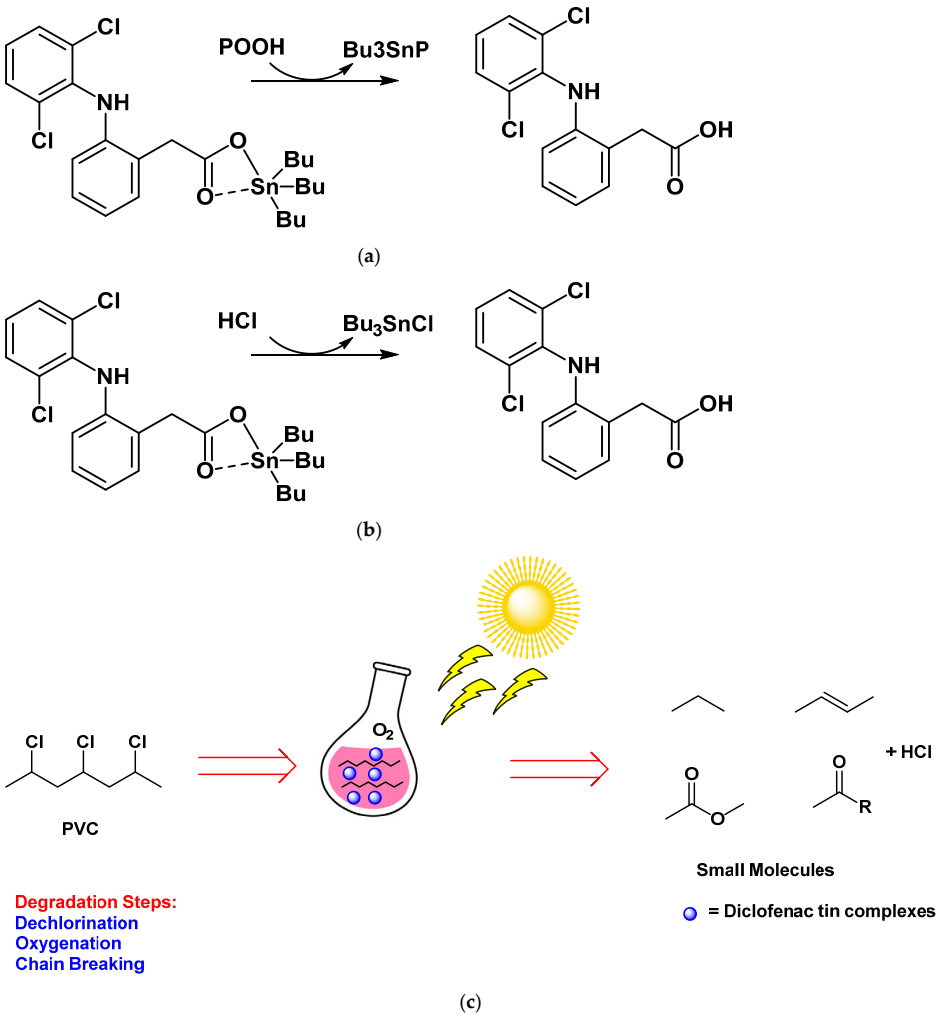


Figure 9. (**a**) Organotin complexes as peroxide decomposers, (**b**) Organotin complexes act as hydrochloride scavengers, and (**c**) Photoprotection process of diclofenac tin (IV) complexes.

The polarized nitrogen and oxygen atoms of the amine and carboxylate groups in tin(IV) complexes, along with the polarized carbon atoms of the PVC C–Cl bonds, may enhance the stabilization of excited-state energy within the polymer chains [29]. Ultraviolet light exposure supplies the energy required for the incorporation of oxygen into these chains. This process commences the degradation of plastics into smaller polymer fragments, which can then be biodegraded by environmental microorganisms. The deterioration of natural plastics occurs initially through photodegradation, succeeded by thermo-oxidative degradation, as seen in Figure 9c. UV absorbers are essential in this process as they absorb harmful radiation and convert it into innocuous heat, thereby inhibiting the generation of free radicals during the initial phases of polymer degradation [30,31].

4. Conclusions

The diclofenac–organotin(IV) complexes synthesized and characterized in this study demonstrated strong potential as effective photostabilizers for PVC. Their aromatic frameworks and heteroatom-rich structures contributed significantly to reducing irradiation-induced degradation, as evidenced by the improved stability of PVC films containing these additives. The results confirm that diclofenac-derived tin complexes can inhibit photodecomposition and enhance the overall durability of PVC under UV exposure. Nevertheless, further investigation into the structure–activity relationships of these complexes is essential to refine their design and maximize their stabilizing efficiency. Continued optimization may lead to the development of highly effective, next-generation stabilizers suitable for industrial applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/physchem6020019/s1. Figure S1: FTIR spectrum of (a) FTIR spectrum of PVC (blank) film before and after irradiation, (b) ligand, (c) Me2SnL2, (d) Ph2SnL2, and (e) Bu3SnL. Figure S2. 1H NMR spectrum of (a) ligand, (b) Me2SnL2, (c) Ph2SnL2, and (d) Bu3SnL. Figure S3. 13C NMR spectrum of (a) ligand, (b) Me2SnL2, (c) Ph2SnL2, and (d) Bu3SnL. Figure S4. 119Sn NMR spectrum of (a) Me2SnL2, (b) Ph2SnL2, and (c) Bu3SnL.

Author Contributions: Conceptualization, H.A.S. and E.Y.; methodology, H.A.S.; software, not applicable; validation, H.A.S. and S.A.A.; formal analysis, H.A.S.; investigation, A.A. and R.A.; resources, T.S.G.; data curation, H.A.S.; writing—original draft preparation, H.A.S. and M.H.A.-M.; writing-review and editing, E.Y., D.S.A., M.K., M.B., T.S.G. and M.S.S.A.; visualization, M.K.; supervision, E.Y.; project administration, M.S.S.A.; funding acquisition, E.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The original contributions presented in this study are included in the article/Supplementary Materials. Further inquiries can be directed to the corresponding author.

Acknowledgments: The authors express their gratitude to Al-Nahrain University for its partial support of this work.

Conflicts of Interest: The authors declare no conflicts of interest.

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