Elucidating the Photoluminescence Quenching in Ensulizole: an Artificial Water Soluble Sunscreen

Muhammad Mubeen 1 · Muhammad Adnan Khalid 1 · Maria Mukhtar 1 · Saba Shahrum 1 · Shanila Zahra 1 · Saima Shabbir 2 · Azhar Iqbal 1

Received: 2 March 2021 / Accepted: 3 May 2021 / Published online: 6 May 2021
© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

Abstract
Employing natural or artificial sunscreens is essential to protect the skin from ultraviolet radiations that cause premature aging and develop melanoma and other forms of skin cancer. The 2-Phenylbenzimidazole-5-sulfonic acid, commonly known as ensulizole is a water-soluble artificial sunscreen that absorb UV-B (280 nm – 315 nm) radiations and protects the skin against the harmful effects of these radiations. We have measured steady-state photoluminescence (SSPL) spectra and photoluminescence (PL) kinetics of this compound in various conditions. Steady-state absorption indicates a strong absorption feature at 303 nm and a weak one at 316 nm that have been identified as \( \pi \rightarrow \pi^* \) and \( n \rightarrow \pi^* \) transitions, respectively. The spectra of PL induced by these absorptions indicate that the PL of ensulizole is less Stokes-shifted in polar solvents and more Stokes-shifted in non-polar solvents. The average PL lifetime of ensulizole is longer in non-polar solvents than in polar solvents and it exhibits the shortest PL lifetime in aqueous medium that maximize its transition efficiency in water. This suggests in non-polar solvents intersystem crossing is the dominant mode of relaxation of the excited \( \pi\pi^* \) state. Furthermore, an increase of pH of ensulizole solution decreases the PL intensity and the lifetime. Stern-Volmer equation is employed to evaluate bimolecular quenching rate constant \( k_q \). The evaluation result suggests the diffusional dynamic mode of PL quenching is operative.

Keywords Sunscreen · Ensulizole · Photoluminescence · Time resolved · Quenching

Introduction
The sunscreens act as protective coating for DNA mutation against UV radiations [1–4]. The extreme sun exposure could cause skin erythema and tanning. This fact has been known for long time ago [5]. However the real mechanism was hitherto unclear [6]. Excessive exposure to the sunlight can perform a major role in degenerative disease in the skin like photocaging and skin cancer [7–12]. It has been proved that ultraviolet (UV) radiations cause erythema solare [13]. This necessitates use of chemical sunscreens for the protection of skin [14–16]. First ever-efficacious commercial UV sunscreen, “Aubre Solaire” [17] was benzylsalicylate. In addition to this, many other effective compounds have been explored as sunscreens that lead to a general adoption of 4-aminobenzoic acid and later benzophenones as sunscreen agents [18]. Nowadays, a number of different UV absorbing molecules find their use in commercial sunscreens [19–21]. There are 27 registered compounds that are used as UV-filter in Europe as sunscreens [8].

Some of the sunscreen components might have a hostile effects on human skin and it is referred as “sunscreen controversy” [19, 22–24], therefore it is necessary to investigate the exact way of action of a sunscreen in order to eliminate its detrimental effects. Sunscreens are formulated to absorb the UV-A (320–400 nm) and UV-B (280–320 nm) [6, 25, 26] components of sunlight. As a result, the possibility of skin cancers such as melanoma or squamous cell carcinoma decreases drastically [27, 28]. Sunscreens in general consist of a substantial carrier oil, photostable inorganic particulates (ZnO and/or TiO2) along with organic molecules having extended conjugation. These conjugated organic molecules provide photo-protection, without any photodegradation and phototoxicity. Numerous organic molecules used in sunscreens
contain aromatic rings conjugated to carbonyl groups like oxybenzone, avobenzone, cinnamates (e.g. ferulic acid and caffeic acid), and salicylates [29–31]. Such molecules provide photo-protection by means of their high UV absorption cross-sections. The absorption of UV radiations leads to electronic excitation and absorbed energy is quickly diffused through intramolecular vibrational energy redistribution (IVR) and dissipates it in the form of heat within the sunscreen [31–33].

2-Phenylbenzimidazole-5-sulfonic acid commonly known as “ensulizole” [34] is an effective and recommended sunscreen agent [7, 35–37] and it is a part of many commercially available sunscreen products [38]. Therefore, it is essential to understand the photophysical properties of ensulizole in order to develop more effective sunscreen products based on this compound. We studied the PL dynamics following excitation at 306 nm for the first time. The steady-state photoluminescence (SSPL) and time-resolved photoluminescence (TRPL) techniques are employed to investigate the PL dynamics of ensulizole both in solid-phase and as well as in solution form in different solvents, for instance, in CCl₄, acetone, water, methanol and ethanol. The PL kinetics demonstrates the average PL lifetime is longer in non-polar solvents than polar solvents. It has also been observed that with an increase in hydrogen ion (H⁺) concentration, PL quenches and the average PL lifetime decreases due to the reduction in delocalization of π-electrons of ensulizole. This leads to the evaluation of bimolecular PL quenching rate constant k_q, which has been estimated 2.945 × 10⁷ M⁻¹ s⁻¹. This work particularly addresses the effects of solvents polarity and the pH on the PL dynamics of ensulizole that have not been explored thoroughly yet. These findings would prove a step forward towards understanding the mechanism of absorbed UV energy dissipation pathways in this important water-soluble sunscreen component.

Materials and Methods

Materials

Ensulizole (98 %) was purchased from Tokyo Chemical Industry (TCI) and was used without any further purification. Deionized water was used for all aqueous-phase measurements. Acetone (Merck, 99.5 %), methanol (Analytical Reagent, 99.9 %) and ethanol (Analytical Reagent, 99.9 %) were purchased from RCI Labscan and CCl₄ (99.8 %) was purchased from Riedel-de Haen and was used as received without any further purification. The aqueous solutions of various pH were prepared by adding the appropriate amount of HCl or NaOH into the stock solution of ensulizole.

Characterization Methods

The liquid samples of ensulizole were prepared in deionized water, CCl₄, ethanol, methanol and acetone for UV-Vis absorption, SSPL and TRPL measurements at room temperature. The concentration of all liquid samples solutions was 1µM. Shimadzu UV-1601 spectrophotometer was used to measure the UV–Vis absorption spectra at room temperature. All the samples were examined using the quartz cuvettes. The SSPL and TRPL measurements were conducted by Pico Quant Fluo Time 300 (FT-300) spectrophotometer as described in our previous work [39–41]. Briefly, the SSPL spectra were measured following excitation at 306 nm with a pulsed LED excitation (PLS-300) source. The pulse duration of PLS-300 is 416 ps and its pulse energy is 0.077 pJ. In order to filter the residual light of excitation source and to avoid second order diffraction a long-pass filter FGL400 was used. The aqueous paste of ensulizole was applied on quartz slide in the form of a thin film and was used for SSPL and TRPL measurements in solid form.

Results and Discussion

The UV-Vis absorption spectra of ensulizole (Fig. 1) in different solvents (CCl₄, acetone, water, methanol, and ethanol) are displayed in Fig. 2a. In a polar neutral medium, ensulizole exists in monoanionic form and its sulfonic acid group donates proton that is accepted by the polar solvents like water, methanol, and ethanol and subsequently stabilize the conjugate base of ensulizole. Removal of one or both protons from ensulizole results in a decrease of localization of electrons, which tends to cause a red-shift in the UV absorption spectrum. The imidazole ring proton does not detach due to the neutral medium. For the removal of the imidazole ring proton, a highly basic medium (pH = 14) is required and that is evidenced by Fig. 2b. A slight difference in the UV spectrum is observed in the case of methanol and ethanol as compared to water. This can be attributed to the electron releasing inductive effect [42] of alkyl groups that stabilizes both the protonated methanol and protonated ethanol.

![Fig. 1 Structural formula of Ensulizole (2-Phenylbenzimidazole-5-sulfonic acid)](image-url)
As the ethyl-group has greater electron donating inductive effect, therefore, the absorption peak of ensulizole in ethanol is broadened and slightly red-shifted than in methanol, which in turn is more red-shifted than water, as it does not offer any such inductive stabilization effect. Acetone is a weakly polar solvent. It does not facilitate the ionization process as polar solvents demonstrate, for instance water, methanol and ethanol. This is manifested by the less solubility of ensulizole in acetone. Therefore, ensulizole shows a blue-shift in UV absorption spectra as compare to water, Fig. 2a. The ensulizole is more soluble CCl₄ due to non-polar interactions but these interactions do not favour the ionization of sulfonic acid group proton of ensulizole. Therefore, ensulizole remains undissociated in CCl₄ and its UV-Vis absorption spectrum exhibits a blue-shift as displayed by Fig. 2a. The reaction Scheme 1 displays the proposed mechanism of proton transfer in various solvents.

Some of the polar solvent molecules are converted into their respective conjugate acids form and remaining free solvent molecules develop hydrogen bonding with ensulizole at specific sites. The hydrogen bonding interaction affects the electronic excitations, in general an increase in solvent

---

**Fig. 2** Comparison of steady-state UV-Vis absorption spectra of Ensulizole a in different solvents and b in water at different pH
polarity causes a blue-shift in n→π* transitions and a red-shift in π→π* transitions [8].

The UV-Vis absorption spectra of ensulizole in water at pH=2 (Fig. 2b) demonstrate in strongly acidic conditions the ensulizole exists as undissociated acid. It exhibits an absorption peak at ~300 nm because of π→π* transition and a shoulder at 314 nm due to n→π* transition. As ensulizole is a weak acid (pKa1 = 4 and pKa2 = 11.9), so its solution is mildly acidic (pH = 6) when dissolved in water. It is the sulfonic acid group proton, which dissociates under these conditions and the absorption spectrum at this pH is slightly red-shifted. Reaction Scheme 2 presents the proposed mechanism of proton transfer in different pH environments.

In highly alkaline medium (i.e., at pH > 12), both the sulfonic acid and imine moieties protons of ensulizole are removed and the absorption peak even further red-shifts at this pH. The red-shift occurs due to increase in the delocalization of the π-electrons. The pronounced red-shift observation following removal of imine proton confirms the N-H group in imidazole ring is the chromophore and controls the photochemistry of ensulizole following excitation at 306 nm, as substantiated by laser flash photolysis experiments [43].

As justified above with the help of UV-Vis measurements that ππ* state along the N-H coordinate of imidazole ring will be excited at 306 nm with pulsed PLS excitation source. Henceforth, all the results of SSPL and TRPL measurements will be discussed after pulsed excitation at 306 nm. The SSPL spectra of ensulizole in solid form as well as those in solution form in different solvents is displayed by Fig. 3a. Following excitation at 306 nm the PL spectrum of ensulizole exhibits a peak at 445 nm in solid form as well as in slightly polar or non-polar solvents, like acetone and CCl4, where there is no or
very weak solute-solvent interactions exist. In polar solvents like methanol, ethanol and water the PL spectra of ensulizole exhibit a pronounced blue-shift and the PL peaks move to 412 nm as compare to slightly polar or non-polar solvent (λ_{emission} = 445 nm) like CCl₄, Fig. 2a. This trend can be attributed to the occurrence of hydrogen bonding between the aforementioned polar solvents and the ensulizole solute molecules.

Polar solvents like water, methanol and ethanol develop hydrogen bonding with ensulizole and due to this effect, non-bonding electrons on the nitrogen and oxygen atoms are engaged with the solvent molecules. This results in increase localisation of non-bonding electrons and consequently a blue-shift in PL spectrum is observed. Slightly polar or non-polar solvents like acetone and CCl₄ are unable to develop hydrogen bonding with the hetero-atoms of ensulizole, so the lone pairs of electrons are unrestricted and enhance the delocalization of π-electrons and causes a red-shift in the PL spectrum. A major evidence in this regard is the SSPL spectrum of ensulizole in the solid-state sample where no solute-solvent interactions are possible. Amongst the polar solvents, SSPL spectra exhibit a slight red-shifted tail, which is more pronounced in ethanol and methanol than in water. This is probably due to the polarity of the solvent and the

---

**Fig. 3** Effect of a various solvents interactions on the PL of ensulizole and b varying pH on the PL of ensulizole in water
delocalization effect, as justified above. The SSPL spectra of ensulizole in non-polar solvents are much broader as compared to the polar solvents. This is attributed to the enhanced delocalization effect in non-polar solvents. A slight blue-shift in the SSPL spectra of ensulizole is observed in the acidic medium as shown in Fig. 3b. This again can be attributed to the fact that the increase in pH results in enhancement of delocalization and these observations are in consistent with the UV-Vis absorption measurements.

In order to assess the lifetime of \( \pi\pi^* \) state the PL kinetics is also measured. The ensulizole samples were excited at 306 nm and the PL decay kinetics was monitored at room temperature. Figure 4a depicts the PL decay kinetics of ensulizole in different solvents. The PLS-306 LED excitation source along with the electronics of time-correlated single photon-counting (TCSPC) setup allow conducting the measurements with a time-resolution of 500 ps. It is a well-known fact that an increase of solute-solvent interaction facilitates the internal conversion process. This leads to a decrease in PL efficiency [44]. Reduction in the PL efficiency is directly related to shortening of PL lifetime. In aforementioned polar solvents, the ensulizole exhibits short PL lifetime and the PL decay kinetics is found to be monoeponential (Fig. 4a), in comparison to the non-polar solvents due to solute-solvent interactions, which are present in former and are absent in the latter. Thus, the polar solvents due to existence of solute-solvent interaction increase the internal conversion (IC) rate and decrease the PL lifetime, confirming the ensulizole can be the an effective sunscreen in polar solvents particularly in water, where the \( \pi\pi^* \) state exhibits the shortest lifetime. To further corroborate this finding, the solvent polarity was gradually decreased. This resulted in enhancement of PL lifetime. In order to eliminate the solvent-solute interactions the measurements were also conducted in the solid film of the ensulizole (Fig. 4b). The measured PL kinetics of all the solution-phase samples is fitted by a suitable exponential decay model (Eq. 1) and the fitting parameters are displayed in Table 1. The solid sample of ensulizole exhibited the longest PL lifetime (\( \tau_{av} = 6.879 \text{ ns} \)) and this can be attributed to the population transfer from the single to triplet state by intersystem crossing (ISC) process. The average PL lifetimes were estimated by Eq. (2) using the time constants and the coefficients extracted from Eq. (1).

\[
Y = Y_0 + \sum_{i=1}^{n} A_i e^{-x_{av} t_i}
\]

\[
\tau_{\text{average}} = \frac{\sum_{i=1}^{n} A_i \tau_i}{A_i}
\]

Here \( A_i, x_0 \) and \( t_i \) are the associated coefficients, time zero and the time constants, respectively. The \( \tau_{av} \) and the extracted fitting parameters from the aforementioned Eqs. (1) & (2) are presented in Table 1.

In order to study the effect of pH on the excited \( \pi\pi^* \) state lifetime, the PL kinetics was also conducted in various pH environments in water as solvent. Figure 4c displays different PL decay kinetics for ensulizole in mono-anionic form i.e., at pH = 6, in molecular form i.e., at pH = 2 and in highly basic medium i.e., at pH = 14. The measured PL kinetics is best fitted by biexponential decay model for pH 2–6 and a unimolecular (monoeponential) decay model for pH 8–14, Table 2. The increase in PL lifetime by increasing the pH from acidic to highly basic medium is due to enhanced stabilization of \( \pi \)-electronic system after removal of the second proton from the imino group. These findings again confirm that imidazole ring is the chromophore of the ensulizole and are in consistent with the steady-state absorption analysis. This inference is also in accordance with previously reported laser flash photolysis experiments, where following excitation at 266 nm the dissociation of imino group and the formation of dianion of ensulizole through double deprotonation has been observed [43]. Although these experiments do not exactly mimic the TRPL measurements performed here, but as justified above the high pH extracts the second H\(^+\) from the imino group that further stabilizes the \( \pi \)-electron system and enhances the PL lifetime.

The removal of the second H\(^+\) and enhancement of the PL lifetime confirms that the photoexcited \( \pi\pi^* \) state along the N-H coordinate of imidazole ring controls the photochemistry of ensulizole following excitation at 306 nm.

A gradual drop in PL intensity of ensulizole is observed with a decrease in pH value from 14 to 2 as shown in Fig. 3b. This reflects a quenching role of hydrogen ions (H\(^+\)) in this process. With increase in H\(^+\) concentration (decrease in pH value), a decrease in PL intensity and average PL lifetime has been observed. By applying Stern-Volmer Eqs. [45, 46] (Eqs. 3 & 4) to the measured PL data, a straight line with intercept equal to one is obtained (Fig. 4d), thus confirming the dynamic and diffusion controlled PL quenching of the ensulizole. The linear fit to the data enabled to evaluate the Stern-Volmer quenching constant \( K_{SV} \), 0.06995 M\(^{-1}\), where \( K_{SV} = k_q \times \tau_o \).

\[
\frac{\tau_0}{\tau} = 1 + K_{SV}[Q]
\]

\[
\frac{\tau_0}{\tau} = 1 + K_q \tau_0[H^+]
\]

Where \([Q]\) is concentration of quencher, \( \tau_o \) is average lifetime in the absence of quencher, \( \tau \) is average lifetime in the presence of quencher and \( k_q \) is bimolecular quenching rate constant (Eq. 4). The estimated
value of bimolecular quenching constant is $2.945 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. In this study, we quantitatively demonstrate the lifetime of $\pi\pi^*$ state locating on N-H coordinate of imidazole ring of ensulizole that strongly depends on the solvent polarity and the pH of the medium. Our future studies will focus on the photochemistry of ensulizole attached semiconductor quantum dots (QDs) to address how the QDs alter the photochemistry of the chromophore, in particular the N-H coordinate.

### Conclusions

The TRPL measurements confirmed the ensulizole could be an effective sunscreen in water because it exhibited shorter PL lifetime as compared to the other solvents. It further demonstrated the average PL lifetime of $\pi\pi^*$ ensulizole was higher in non-polar solvents than in polar solvents particularly in H$_2$O. This was attributed to solute-solvent interactions, which were present in polar

---

**Table 1** The fitting parameters extracted from a unimolecular (monoexponential), biexponential, triexponential and tetraexponential decay models for ensulizole in different solvents

| Sample ID        | $\tau_1$ (ns) | $\tau_2$ (ns) | $\tau_3$ (ns) | $\tau_4$ (ns) | $\tau$(Average) (ns) |
|------------------|---------------|---------------|---------------|---------------|---------------------|
| Ensulizole film  | 1849.5        | 10,958        | 1.757         | 1302.5        | 6.879               |
| CCl$_4$          | 0.133         | 0.803         | 1.869         | 43.363        | 5.918               |
| Acetone          | 0.118         | 28.762        | 1.567         | ---           | 4.763               |
| Ethanol          | 1             | 2.847         | ---           | ---           | 2.847               |
| Methanol         | 1             | 2.505         | ---           | ---           | 2.505               |
| Water            | 1             | 1.688         | ---           | ---           | 1.688               |
solvents and absent in non-polar solvents. The polar solvents encouraged the IC and reduced the lifetime of the excited \( \pi\pi^* \) state. A solid evidence in this regard was the much longer PL lifetime (\( \tau_{av} = 6.879 \) ns) of ensulizole in the solid phase. The measured PL kinetics also suggested that in non-polar solvents and in solid phase the probability of ISC increased by populating the triplet state thus resulting in the enhancement of the PL lifetime. It was observed that with decrease in pH value from 14 to 2, the PL intensity and hence average PL life time of ensulizole both reduced. This confirmed the H\(^+\) behaved as PL quencher and by applying Stern-Volmer equation, the dynamical quenching rate constant, K\(_q\) = 2.945 \times 10^{7} \text{ M}^{-1} \text{ s}^{-1} was estimated. These findings suggest the PL and hence the photo-chemistry of ensulizole after excitation at 306 nm is greatly influenced by the pH and the solvent polarity and the repercussions of which will help to improve the understanding of underlying photochemistry of water soluble ensulizole and to increase its action in acidic and basic media.

**Acknowledgements** This work was performed within the Department of Chemistry Quaid-i-Azam University Islamabad. The authors gratefully acknowledge financial support by Higher Education Commission (HEC) Pakistan through research/equipment grants 20-3071/NRPU/R&D/HEC/13 and 6976/Federal/NRPU/R&D/HEC/2017.

**Author Contributions** All authors contribute to the study of conception and design. Muhammad Mubeen performed the experiments and wrote the initial draft of the manuscript. Muhammad Adnan Khalid, Maria Mukhtar, Saba Shahrum and Sanila Zahra helped to conduct the experiments and data acquisition. Saima Shabbir commented on the manuscript and revised. Azhar Iqbal perceived the idea, acquired the funding, and supervised the work and writing of the manuscript.

**Funding** This study was supported by Higher Education Commission (HEC) Pakistan through research/equipment grants 20-3071/NRPU/R&D/HEC/13 and 6976/Federal/NRPU/R&D/HEC/2017.

**Table 2** The fitting parameters extracted from a unimolecular (monoeponential), biexponential decay kinetics models for ensulizole at different pH

| Sr. no. | pH | A\(_1\) | \(\tau_{1}(\text{ns})\) | A\(_2\) | \(\tau_{2}(\text{ns})\) | \(\tau_{(\text{Average})}(\text{ns})\) | \(\tau_{av}/\tau\) |
|---------|----|--------|----------------|--------|----------------|---------------------------------|----------------|
| 1.      | 2  | 17,283 | 1.367          | 187.5  | 3.481          | 1.389                           | 1.709          |
| 2.      | 4  | 15,857 | 1.485          | 27.51  | 16.38          | 1.511                           | 1.572          |
| 3.      | 6  | 16,262 | 1.678          | 17.42  | 14.84          | 1.692                           | 1.404          |
| 4.      | 8  | 15009.5| 1.910          | ---    | ---            | 1.911                           | 1.243          |
| 5.      | 10 | 15,551 | 2.056          | ---    | ---            | 2.056                           | 1.156          |
| 6.      | 12 | 15522.4| 2.347          | ---    | ---            | 2.347                           | 1.012          |
| 7.      | 14 | 15,190 | 2.376          | ---    | ---            | 2.375                           | 1              |

**Data Availability** All data generated or analyzed during this study are included.

**Code Availability** All data were obtained using word, origin and Chemdraw.

**Declarations**

**Conflicts of Interests/Competing Interests** There are no conflicts of interest to declare.

**Ethics Approval** Not applicable.

**Consent to Participate** Not applicable.

**Consent of Publication** Not applicable.

**References**

1. Bais AF, Lucas RM, Borman JF, Williamson CE, Sulzberger B, Austin AT, Wilson SR, Andrady AL, Bernhard G, McKenzie RL (2018) Environmental effects of ozone depletion, UV radiation and interactions with climate change: UNEP Environmental Effects Assessment Panel, update 2017. Photochem Photobiol Sci 17: 127–179
2. Bernhard GH, Neale RE, Barnes PW, Neale P, Zepp RG, Wilson SR, Andrady AL, Bais AF, McKenzie R, Aucamp P (2020) Environmental effects of stratospheric ozone depletion, UV radiation and interactions with climate change: UNEP Environmental Effects Assessment Panel, update 2019. Photochem Photobiol Sci 19:542–584
3. Kao M-H, Venkatraman RK, Snea M, Wilton M, Orr-Ewing AJ (2021) Influence of the solvent environment on the ultrafast relaxation pathways of a sunscreen molecule diethylamino hydroxybenzoyl hexyl benzoxate. J Phys Chem A 125:636–645
4. Bacardit A, Cartoixà X (2020) Revisiting the role of irradiance in the determination of sunscreens’ sun protection factor. J Phys Chem Lett 11:1209–1214
5. Serrano Jareño MA, Moreno J (2013) Erythemal ultraviolet solar radiation doses received by young skiers. Photochem Photobiol Sci 12:1976–1983
6. Baker LA, Clark SL, Habershon S, Stavros VG (2017) Ultrafast transient absorption spectroscopy of the sunscreen constituent Ethylhexyl triazine. J Phys Chem Lett 8:2113–2118
7. Inbaraj JJ, Bilski P, Chignell CF (2002) Photophysical and photo-chemical studies of 2-phenylbenzimidazole and UVB sunscreen 2-phenylbenzimidazol-5-sulfonic acid. Photochem Photobiol 75: 107–116
8. Herzog B, Amorós-Galicia L, Sohn M, Hofer M, Quass K, Giesinger J (2019) Analysis of photokinetics of 2'-ethylhexyl-4'-methoxy cinnamate in sunscreens. Photochem Photobiol Sci 18: 1773–1781
9. Dondi D, Albini A, Serpone N (2006) Interactions between different solar UVB/UVA filters contained in commercial suncreams and consequent loss of UV protection. Photochem Photobiol Sci 5:835–843
10. Lewicka ZA, William WY, Oliva BL, Contreras EQ, Colvin VL (2013) Photochemical behavior of nanoscale TiO2 and ZnO sunscreen ingredients. J Photochem Photobiol A 263:24–33
11. Wright CY, du Preez DJ, Martineigh BS, Allen MW, Millar DA, Wemecke B, Blesic S (2020) A comparison of solar ultraviolet...
