Short-lived and nonphosphorescent triplet state of Mexoryl SX, a UV-A sunscreen

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Abstract

Mexoryl SX (terephthalylidene-3,3'-dicamphor-10,10'-disulfonic acid, Ecamsule) is a water-soluble UV-A absorber. The near-IR phosphorescence spectrum of singlet oxygen generated by photosensitization with Mexoryl SX was not observed in air-saturated water. On the other hand, the time-resolved near-IR phosphorescence spectrum was observed in oxygen-saturated phosphate buffer (pH 7.4). The quantum yield of the singlet oxygen generation (Φ_{Δ}) was determined to be 0.0021 ± 0.0005 . The ability of Mexoryl SX as a photosensitizer is quite low. The question arises as to the quite low Φ_{Δ} value. No phosphorescence was detectable from Mexoryl SX in ethanol at 77 K. We elucidated the nature of the lowest excited triplet (T_1) state of Mexoryl SX using a time-resolved EPR technique because this technique is powerful for the study of short-lived and non-phosphorescent T_1 molecules. The strong time-resolved EPR signals were observed. This fact shows that a considerable proportion of the lowest excited singlet (S_1) state molecules undergoes intersystem crossing (ISC) to the T_1 state and the deactivation process of the T_1 state is mainly radiationless. The observed zero-filed splitting parameters, T_1 lifetime and $S_1 \rightarrow T_1$ ISC anisotropy suggest that the T_1 state can be regarded as a ${}^3n\pi^* \rightarrow {}^3\pi\pi^*$ mixing state in character and the two unpaired electrons in the T_1 state do not localize on (4-methylbenzylidene)camphor, a closely related component. Although the shorter T_1 lifetime (47 ns) prevents T_1 state quenching by ground-state oxygen, the ${}^3n\pi^*$ character may contribute something to the low Φ_{Δ} value.

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1. Introduction

Solar UV radiation exhibits a number of harmful effects on human skin and eye. Numerous scientists the world over have been indicating a high correlation between solar UV exposure and skin cancer, premature photoaging, photodermatoses and accumulation of wrinkles [1–4]. They have also been suggesting a strong correlation between UV exposure and the development of cataract, keratopathy and pterygium [5]. Excessive exposure to solar UV radiation has resulted in an increasing demand to protect human skin and eye against the detrimental effects of solar UV radiation [5–7].

Sunscreen should protect not only against UV-B (280–320 nm) radiation, but also against the harmful effects of the more deeply penetrating UV-A (320–400 nm) radiation. UV-A radiation indirectly damage DNA of keratinocytes via free radical-mediated pathway [6,7]. UV-A is absorbed by endogenous photosensitizers, such as porphyrins, riboflavin and heme, which induces the generation of reactive oxygen species [6].

Mexoryl SX (terephthalylidene-3,3'-dicamphor-10,10'-disulfonic acid, Ecamsule, Scheme 1) is a water-soluble UV-A absorber [8]. This UV-A absorber has been a proprietary absorber from L'Oréal. Mexoryl SX is a (4-methylbenzylidene)camphor (4-MBC, Scheme 1) sulfonic acid derivative [9]. Mexoryl SX shows excellent photostability under solar UV irradiation. Although it is not approved in the USA, it is widely used in sunscreen products (up to 10%) in Australia, ASEAN, Canada, EU, Japan and MERCOSUR [10].

A sunscreen molecule absorbs UV radiation and is photoexcited to a higher energy state which is a potentially reactive state. An ideal sunscreen molecule is expected to have the ability to dissipate the absorbed UV energy rapidly and relax back to the ground state without forming any harmful species. However, very little is known about the excited states of Mexoryl SX. To the best of our knowledge only one study was reported by Cantrell et al. in scientific literature [11]. They reported the results of a nanosecond laser flash photolysis investigation of Mexoryl SX.

Scheme 1. Molecular structures and principal axes (x , y , z) of the ZFS tensor chosen for Mexoryl SX and 4-MBC.

In this paper we report the results of time-resolved near-IR phosphorescence studies of Mexoryl SX-photosensitized singlet oxygen generation in phosphate buffer (pH 7.4) at room temperature and time-resolved electron paramagnetic resonance (EPR) studies of the lowest excited triplet (T_1) state of Mexoryl SX.

2. Experimental

2.1. Chemicals

Phenalenone was obtained from Aldrich and used as received. Ethanol (Super Special Grade) and phosphate buffer solution (0.1 mol dm^{-3} , pH 7.4) were obtained from FUJIFILM Wako and used as received. Mexoryl SX was donated by Shiseido Co., Ltd.

2.2. Optical measurements

The UV absorption spectra were measured with a JASCO V-550 spectrometer. The fluorescence spectra were measured with a JASCO FP-6500 spectrofluorometer. For the phosphorescence measurements, the samples were excited with an Asahi Spectra REX-250 Hg lamp. The emissions from the samples were passed through a Horiba Jobin Yvon H-20VIS spectrometer and detected by a Hamamatsu Photonics R374 photomultiplier tube.

The details of the time-resolved near-IR phosphorescence measurements are the same as those reported previously [12]. Sample solutions were excited with a Continuum Surelite Nd:YAG laser (355 nm). The emissions were passed through an Asahi Technoglass IR-D80A glass filter (transmits the wavelength 800–3000 nm) and a Shimadzu SPG-120IR monochromator and then detected by a Hamamatsu Photonics H10330A-45 near-IR photomultiplier tube module equipped with a Hamamatsu Photonics C999 amplifier unit (10 MHz). The output signal was fed into a Tektronix TDS 3012C digital phosphor oscilloscope (100 MHz) and a Stanford Research SR250 boxcar integrator equipped with a Keyence NR-2000 data acquisition system.

2.3. EPR measurements

The experimental setup for the EPR measurements is essentially the same as that reported previously [13,14]. The steady-state EPR measurements were carried out using a JEOL-JES-FE1XG X-band spectrometer. A Canrad-Hanovia Xe-Hg lamp equipped with an Asahi Technoglass UV-D33S glass filter (transmits the wavelength 250–400 nm), 5 cm of water filter and a Copal DC-494 electromechanical shutter was used as an excitation source. The external magnetic field was calibrated with an Echo Electronics EFM-2000 proton NMR gauss meter. The output signal was fed into an Electronica ELK-5125 waveform storage and a personal computer. For the lifetime measurements, the signals were averaged 512 traces to improve the S/N ratio.

The time-resolved EPR measurements were carried out using a JEOL-JES-FA200 X-band spectrometer without magnetic field modulation. The external magnetic field was calibrated with an Echo Electronics EFM-2000AX proton NMR gauss meter. The samples were excited with the Continuum Surelite Nd:YAG laser (355 nm, repetition rate 10 Hz). For the magnetophotoselection experiments, a Glan-Thompson polarizer was placed between the laser and the sample to polarize the laser light. The output of the diode of the EPR spectrometer was fed into a Tektronix TDS 3032B digital phosphor oscilloscope (300 MHz) and the Stanford Research SR250 boxcar integrator.

3. Results and discussion

3.1. UV absorption and Emission spectra

The UV absorption spectrum of Mexoryl SX in phosphate buffer (pH 7.4), shown in Fig. 1, is similar to that observed in water by Cantrell et al. [11]. The absorption maximum was observed at 345 nm. DFT calculations were carried out to analyse the UV absorption spectrum using Spartan'18 version 1.2.0 (Wavefunction Inc., CA, USA). Fig. 2 shows the frontier molecular orbitals calculated by Spartan'18 at the B3LYP/6-31G* level in vacuum. The principal excitation leading to absorption in the UV-A region of the spectrum was characterized as being a HOMO–LUMO transition.

No fluorescence was detectable from Mexoryl SX in ethanol at 77 K. Cantrell et al. reported that Mexoryl SX is nonfluorescent in ethanol or water, but weakly fluorescent in acetonitrile at room temperature [11]. The lowest excited singlet (S_1) state is nonfluorescent or very weakly fluorescent in ethanol. We tried to observe the phosphorescence spectrum of Mexoryl SX in ethanol at 77 K using a phosphoroscope with a 2 ms dead time. However, no phosphorescence was detectable from Mexoryl SX. As is mentioned in the

Fig. 1. (a) UV absorption spectrum of Mexoryl SX in phosphate buffer (pH 7.4) at 25 °C.

Fig. 2. Frontier molecular orbitals of Mexoryl SX obtained by DFT calculations. Calculated by Spartan'18 at the B3LYP/6-31G* level in vacuum.

following section, the lifetime of the T_1 state of Mexoryl SX is shorter than 10 ms (longer than 2 ms) in ethanol at 77 K. The T_1 state is nonphosphorescent or very weakly phosphorescent.

3.2. Near-IR phosphorescence of singlet oxygen

It is well known that the most important method of generating singlet oxygen, $^1O_2(^1\Delta_g)$, in solution is quenching of the T_1 states of organic molecules by ground-state oxygen, $^3O_2(^3\Sigma_g^-)$. However, the near-IR phosphorescence spectrum of singlet oxygen generated by photosensitization with Mexoryl SX was too

Table 1

Calculated $\lambda_{\max}$, oscillator strengths and main transitions of Mexoryl SX obtained by TD-DFT calculations ^a

$\lambda_{\max}$ (nm)	Oscillator strength	Main transition
366.3	1.3406	HOMO to LUMO (93%)
353.5	0.0004	HOMO-2 to LUMO (81%)
353.0	0.1244	HOMO-1 to LUMO (76%)
303.2	0.0111	HOMO-3 to LUMO (88%)

^a Calculated by Spartan'18 at the B3LYP/6-31G* level in vacuum.

weak to be observed in air-saturated water at room temperature. We tried to observe the singlet oxygen phosphorescence in oxygen-saturated phosphate buffer (pH 7.4). The concentrations of dissolved oxygen in air-saturated and oxygen-saturated water at 25 °C are 0.27 and 1.27 mmol dm⁻³, respectively [15]. The wavelength of the singlet oxygen phosphorescence peak (about 1274 nm), shown in Fig. 3, is in good agreement with that reported previously in D₂O by Schmidt (1273.9 nm) [16]. The observed lifetime of singlet oxygen generated by Mexoryl SX-photosensitization, 3.6 μs, is in good agreement with the previously reported value 3.6 μs (in air-saturated water) [17].

The use of the nanosecond pulsed laser allows us to analyse the time profile of singlet oxygen phosphorescence after laser shots. The rise and decay times of singlet oxygen phosphorescence, I_t , are given by the following biexponential function [17–19]:

$$I_t = c \times \Phi_{\Delta} \{ \tau_{\Delta} / (\tau_{\Delta} - \tau_T) \} [\exp(-t/\tau_{\Delta}) - \exp(-t/\tau_T)] \quad (1)$$

where Φ_{Δ} is a quantum yield of singlet oxygen generation; τ_{Δ} and τ_T are a lifetime of singlet oxygen and a T₁ lifetime of a photosensitizer, respectively ($\tau_T \neq \tau_{\Delta}$). The proportionality constant c was used to fit Eq. (1) into the actual time profile. The time position $t_{\max}$ of the relative phosphorescence maximum is given as follows:

$$t_{\max} = (\ln \tau_{\Delta} - \ln \tau_T) / (\tau_T^{-1} - \tau_{\Delta}^{-1}). \quad (2)$$

We should be careful in estimating the Φ_{Δ} values. The phosphorescence maximum depends on τ_{Δ} and τ_T and is not proportional to Φ_{Δ} [20,21].

Fig. 3. Time-resolved phosphorescence spectrum of singlet oxygen generated by excitation of Mexoryl SX in oxygen-saturated phosphate buffer (pH 7.4) at 25 °C. The sampling times were set at 1.5–5.5 μs after the 355 nm YAG laser pulse.

Using phenalenone as a reference photosensitizer, the value of Φ_{Δ} by Mexoryl SX was determined in oxygen-saturated phosphate buffer (pH 7.4). Phenalenone is a water-soluble photosensitizer with Φ_{Δ} of 0.98 [22,23]. A sample and a reference should be measured under exactly the same conditions. The absorbance at 355 nm and energy of the laser pulse for Mexoryl SX were the same as those for phenalenone, 0.84 and 10 mJ, respectively. Fig. 4 shows the time profiles of the phosphorescence intensity of singlet oxygen generated by excitation of phenalenone and Mexoryl SX in oxygen-saturated phosphate buffer (pH 7.4) at 25 °C. In order to observe the initial phosphorescence intensity precisely, the background should be eliminated from the phosphorescence of singlet oxygen. The average of the time profiles at 1200 nm and 1350 nm were subtracted from the time profile at 1274 nm, as shown in Figs. S1 and S2 (see Supplementary Material). The results are shown in Fig. 4.

Fig. 4. Time profiles of the phosphorescence intensity of singlet oxygen generated by excitation of (a) phenalenone and (b) Mexoryl SX in oxygen-saturated phosphate buffer (pH 7.4) at 25 °C. Computer-simulated time profiles (solid lines) obtained with (a) $c = 1.17$ V, $\Phi_{\Delta} = 0.98$, $\tau_{\Delta} = 3.5$ μ s and $\tau_T = 0.45$ μ s, and (b) $c = 1.17$ V, $\Phi_{\Delta} = 0.0021$, $\tau_{\Delta} = 3.6$ μ s and $\tau_T = 0.04$ μ s.

The solid lines in Fig. 4 show the time profiles of the phosphorescence intensity calculated using Eq. (1). The τ_T value of Mexoryl SX was set at 0.04 μs since T_1 lifetime of Mexoryl SX in oxygen-saturated water was determined to be 0.04 μs at room temperature through the measurements of transient absorption [11]. From the computer-simulated time profiles shown in Fig. 4 (solid lines), the Φ_Δ value by Mexoryl SX was estimated to be 0.0021 ± 0.0005 . The ability of Mexoryl SX as a photosensitizer for the singlet oxygen generation is quite low.

3.3. EPR spectra

The question arises as to the quite low Φ_Δ value. We tried to elucidate the nature of the T_1 state of Mexoryl SX through measurements of EPR spectra since the T_1 state is nonphosphorescent or very weakly phosphorescent. A time-resolved EPR technique with pulsed laser excitation is a powerful tool for the study of short-lived and very weakly phosphorescent T_1 molecules [24]. Ethanol was used as a solvent for EPR and phosphorescence measurements at 77 K because the cracking frequency at 77 K is low, 10% [15]. On the other hand, it is difficult to make water form clear rigid glasses (optically clear frozen solvent) at 77 K.

The EPR spectra of the T_1 state in an external magnetic field $\mathbf{B}$ are analyzed in terms of the following spin Hamiltonian:

$$\begin{aligned} H_S &= g\mu_B \mathbf{B} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} \\ &= g\mu_B \mathbf{B} \cdot \mathbf{S} - XS_x^2 - YS_y^2 - ZS_z^2 \\ &= g\mu_B \mathbf{B} \cdot \mathbf{S} + D[S_z^2 - (1/3)\mathbf{S}^2] + E(S_x^2 - S_y^2). \end{aligned} \quad (3)$$

In Eq. (3), $\mathbf{D}$ is a fine-structure tensor of principal values of X , Y and Z . The relation between the zero-field splitting (ZFS) parameters (D and E) and the principal values is $D = -3Z/2$ and $E = (Y - X)/2$. The anisotropy of the g tensor is so small that it is often treated as a free electron g value. The principal axes (x , y , z) of the $\mathbf{D}$ tensor relative to the molecular axes of Mexoryl SX are not known because the molecular symmetry of Mexoryl SX is poor. The skeleton of Mexoryl SX is carbonyl, ethylenic and phenyl groups. Assuming the molecular structure of the skeleton in the T_1 state to be planar in rigid ethanol solution at 77 K, the principal axes were taken to be as shown in Scheme 1. The x -axis deviates by an angle of θ from the L -axis. The L -axis was taken to be parallel to the single bonds between the phenyl and ethylenic groups.

The steady-state EPR spectrum of the T_1 state of Mexoryl SX in ethanol at 77 K was observed using a Canrad-Hanovia Xe-Hg lamp (1 kW), as shown in Fig. 5a. The resonance field of the $B_{\min}$ signal gives the value of D^* through the following equation [25].

$$D^* = \{(3/4)(h\nu)^2 - 3(g\mu_B B_{\min})^2\}^{1/2} \quad (4)$$

Fig. 5. (a) Steady-state EPR spectrum for the T_1 state of Mexoryl SX in ethanol at 77 K. (b) Time profile of the steady-state EPR $B_{\min}$ signal at 153.5 mT.

where

$$D^* = (D^2 + 3E^2)^{1/2} \quad (5)$$

h and ν have their usual meaning. The T_1 lifetime obtained from the decay of the steady-state $B_{\min}$ signal at 153.5 mT is shorter than 10 ms, as shown in Fig. 4b. The value of D^* was estimated to be 0.0926 cm^{-1} using Eq. (4). The $\Delta M_S = \pm 1$ transition signals were not observed in the steady-state EPR measurements. This is due to the short lifetime of the T_1 state.

On the other hand, the $\Delta M_S = \pm 1$ transition signals are fairly strong in the time-resolved EPR measurements, as shown in Fig. 6b. In general, the intensity of the time-resolved EPR signal does not depend on the T_1 lifetime. It depends on the anisotropy in the $S_1 \rightarrow T_1$ intersystem crossing (ISC). This is the reason why the EPR $\Delta M_S = \pm 1$ transition signals were observed in the time-resolved measurements. Therefore, the assignment of the observed $\Delta M_S = \pm 1$ transition signals was carried out for the time-resolved spectrum using the magnetophotoselection method. The time-resolved EPR spectra for the T_1 state of

Mexoryl SX obtained with $\mathbf{B}||\mathbf{E}$ and $\mathbf{B}\perp\mathbf{E}$ are shown in Fig. 6d and e. Here $\mathbf{E}$ denotes the electric vector of the laser light. Although the direction of the transition moment of Mexoryl SX at 355 nm has not yet been determined experimentally, we assume that the transition moment is the same as that of *trans*-cinnamic acid. The polarized UV absorption spectra of *trans*-cinnamic acid show that in-plane long-axis-polarized absorption takes place dominantly at the longest wavelength band [26]. The in-plane long-axis-polarized absorption at 355 nm is also suggested by the HOMO–LUMO transition shown in Fig. 2. As is clearly seen in Fig. 6d and e, the intensity of X signals is relatively strong with $\mathbf{B}||\mathbf{E}$, while the intensity of Y and Z signals is strong with $\mathbf{B}\perp\mathbf{E}$. As a result, the absolute value of X is larger than those of Y and Z ($|X| > |Z|$, $|Y|$ and $|D| < 3|E|$).

The problem we are faced with is the signs of D and E . The ZFS parameters D and E are calculated from the following equations:

$$D = (\mu_0/4\pi)(3/4)(g\mu_B)^2 \int \Phi(\mathbf{r}_1, \mathbf{r}_2) [(r_{12}^2 - 3z_{12}^2)/r_{12}^5] \Phi(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2 \quad (6)$$

$$E = (\mu_0/4\pi)(3/4)(g\mu_B)^2 \int \Phi(\mathbf{r}_1, \mathbf{r}_2) [(y_{12}^2 - x_{12}^2)/r_{12}^5] \Phi(\mathbf{r}_1, \mathbf{r}_2) d\tau_1 d\tau_2. \quad (7)$$

Here, $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is the open shell orbital wavefunction of the T_1 state. The D^* value and T_1 lifetime suggest that the T_1 state possesses mainly a $^3\pi\pi^*$ character. As is known comprehensively, T_z sublevels are the lowest in energy for $^3\pi\pi^*$ states [27]. Consequently, the order of the T_1 sublevels was determined to be $T_x > 0 > T_y > T_z$ in energy. The signs of D and E are positive and negative, respectively. This is consistent with the signs of D and E expected from the distribution of the two unpaired electrons estimated from the HOMO and LUMO shown in Fig. 2. We can reasonably assign all the observed signals as in Fig. 6.

The D and E values listed in Table 2 were obtained from the six stationary fields of the $\Delta M_S = \pm 1$ transition signals using the following equations [28,29].

$$|X| = (1/6h\nu) (g\mu_B)^2 (B_{x2}^2 - B_{x1}^2) \quad (8)$$

$$|Y| = (1/6h\nu) (g\mu_B)^2 (B_{y2}^2 - B_{y1}^2) \quad (9)$$

$$|Z| = (1/6h\nu) (g\mu_B)^2 (B_{z2}^2 - B_{z1}^2) \quad (10)$$

where B_{i1} and B_{i2} ($i = x, y, z$) are the low and high stationary fields of the $\Delta M_S = \pm 1$ transition signals, respectively. The D^* value calculated from the observed D and E values using Eq. (5), 0.0919 cm^{-1} , is in good agreement with that obtained from the steady-state EPR $B_{\min}$ signals using Equation (4), 0.0926 cm^{-1} .

Fig. 6. Computer-simulated (a) steady-state and (c) time-resolved EPR spectra obtained by using $D = 0.0743 \text{ cm}^{-1}$, $E = -0.0312 \text{ cm}^{-1}$ and $(P_x - P_z) : (P_y - P_z) = 0.15 : 0.85$. Time-resolved EPR spectra for the T_1 state of Mexoryl SX in ethanol at 77 K (b) with nonpolarized light and polarized light (d) with $B \parallel E$ and (e) with $B \perp E$. The sampling times were set at 0.3–0.8 μs after the 355 nm laser pulse.

The time-resolved EPR spectrum shows the AEA/EAE polarization pattern of the $\Delta M_S = \pm 1$ transition signals. A and E denote an absorption and an emission of a microwave, respectively. The observed EPR spectra were simulated with the observed ZFS parameters, microwave frequency of 9.218 GHz and a Gaussian linewidth parameter of 2.0 mT. The simulations were carried out using a homemade program (see Supplementary Material). The results are shown in Fig. 6a and c.

Three spin sublevels of the T_1 state couple with different singlet states via spin–orbit couplings. Consequently, the ISC rate constants to the three spin sublevels are different. The time-resolved EPR spectra were analyzed in terms of the spin Hamiltonian taking account of the relative population ratio in the spin sublevels (P_x , P_y and P_z). The population ratio was estimated by the computer simulation, as shown in Fig. 6c. The relative populating rates were estimated to be $(P_x - P_z) : (P_y - P_z) = 0.15 : 0.85$. The $S_1 \rightarrow T_1$ ISC of Mexoryl SX is highly anisotropic. We can confirm the facts that the EPR signal of Mexoryl SX with a short T_1 lifetime is weak in the steady-state measurements but strong in the time-resolved measurements.

An ordinary steady-state EPR technique is adequate to determine T_1 lifetimes longer than several milliseconds. One can determine the T_1 lifetimes from an analysis of the time profile of a time-resolved EPR signal, when the spin-lattice relaxation rates are negligible compared with the T_1 decay rates [24]. The spin-lattice relaxation rates are on the order of microseconds at 77 K [24,31]. The T_1 lifetime of Mexoryl SX should be determined through measurements of steady-state EPR signals although the time-resolved EPR signals are much stronger than the steady-state EPR signals.

The steady-state and time-resolved EPR measurements show that a considerable proportion of the S_1 state Mexoryl SX molecules undergoes ISC to the T_1 state, although at present we have no data on the quantum yield of $S_1 \rightarrow T_1$ ISC in ethanol at 77 K. It is impossible to determine absolute quantum yields of

$S_1 \rightarrow T_1$ ISC by means of the time-resolved EPR spectroscopy. Not only the concentration of T_1 molecules but also the ZFS values affects the intensity of the steady-state EPR $B_{\min}$ signal [31]. The anisotropy in the ISC also affects the intensity of the time-resolved EPR signal [24]. Therefore, it is difficult to determine the quantum yield of $S_1 \rightarrow T_1$ ISC through the measurements of EPR spectra.

3.4. Nature of the lowest excited triplet state

We tried to discuss the observed short T_1 lifetime and highly anisotropic triplet sublevel populating rates of Mexoryl SX in terms of mixing between $^3n\pi^*$ and $^3\pi\pi^*$ states. The TD-DFT calculations suggest that the HOMO–1 to LUMO transition corresponds to an $n\pi^*$ state. In general, the $S_1 \rightarrow T_1$ ISC rates to the three T_1 sublevels are not highly anisotropic for pure $^3\pi\pi^*$ states of aromatic hydrocarbons [27]. On the other hand, they are highly anisotropic for aromatic carbonyls, where $^3n\pi^*$ and $^3\pi\pi^*$ mixing enhances the anisotropy in the $S_1 \rightarrow T_1$ ISC rates to the three T_1 sublevels. The $^3n\pi^*$ character mixed into the $^3\pi\pi^*$ state shortens the T_1 lifetime [24,32].

The T_1 sublevel with the large $S_1 \rightarrow T_1$ ISC rate is T_z for aromatic carbonyls (z is along the C=O direction) [27]. The carbonyl oxygen atom has a large spin-orbit coupling constant and the $^1,^3n\pi^*$ states play an important role in the $S_1 \rightarrow T_1$ ISC process. The molecular symmetry of Mexoryl SX is poor and the local symmetry of the carbonyl moiety is important in determining the $S_1 \rightarrow T_1$ ISC process. As shown in Scheme 1, the deviation of the y -axis from the C=O direction is $\theta - 30^\circ$. One can expect [33]

$$P_x : P_y = \sin^2(\theta - 30^\circ) : \cos^2(\theta - 30^\circ). \quad (11)$$

In the $^3\pi\pi^*$ aromatic molecules with planar molecular structures, the out-of-plane sublevel is much less active in the $S_1 \rightarrow T_1$ ISC process than in-plane sublevels [27,34]. We expect in a first approximation that $(P_x - P_z) : (P_y - P_z)$ is given by

$$(P_x - P_z) : (P_y - P_z) = 0.15 : 0.85 \approx P_x : P_y = \sin^2(\theta - 30^\circ) : \cos^2(\theta - 30^\circ). \quad (12)$$

From Eq. (12) the value θ is estimated to be 53° . The deviation of the y -axis from the C=O direction is estimated to be 23° . The principal axis of the ZFS tensor close to the C=O direction is y in Mexoryl SX. Therefore, the T_1 sublevel preferentially populated by $S_1 \rightarrow T_1$ ISC is expected to be T_y as observed. The observed T_1 lifetime (shorter than 10 ms) and anisotropy in the $S_1 \rightarrow T_1$ ISC rates are explained in terms of the mixing of the $^3n\pi^*$ and $^3\pi\pi^*$ states in the T_1 state of Mexoryl SX.

The fraction of T_1 molecules quenched by ground-state oxygen that gives singlet oxygen is denoted by S_Δ [35,36]. Many values of S_Δ have been reported [35,36]. In general, the $T_1(\pi\pi^*)$ states of polynuclear aromatics are highly efficient at generating singlet oxygen, frequently with $S_\Delta \geq 0.8$. For the $T_1(n\pi^*)$ states of aromatic ketones S_Δ is generally low, $S_\Delta \sim 0.3$ [35,36]. In Ar-saturated aqueous solution the T_1 lifetime

Table 2

ZFS parameters (D , E , D^* , D^{**}), T_1 lifetimes (τ), relative populating rates (P_x , P_y , P_z) and quantum yields of singlet oxygen generation (Φ_Δ) in ethanol at 77 K

Molecule	D (cm ⁻¹)	E (cm ⁻¹)	D^* ^a (cm ⁻¹)	D^{**b} (cm ⁻¹)	τ^c (ms)	$(P_x - P_z) : (P_y - P_z)$	Φ_Δ
Mexoryl SX	0.0743	-0.0312	0.0919	0.0926	< 10	0.15 : 0.85	0.0021 $\pm$ 0.0005 ^d
4-MBC ^e	0.0901	-0.0498	0.1247	0.124	17	0.10 : 0.90	0.05 ^f

^a $D^* = (D^2 + 3E^2)^{1/2}$. ^b Obtained from the EPR $B_{\min}$ signal. ^c Obtained from the decay of the EPR $B_{\min}$ signal. ^d In oxygen-saturated phosphate buffer (pH 7.4) at 25 °C. ^e From ref. 13. ^f In air-saturated ethanol at 25 °C.

of Mexoryl SX (47 ns) is shorter than in Ar-saturated acetonitrile (120 ns) [11]. Although the shorter T_1 lifetime in aqueous solution prevents T_1 state quenching by ground-state oxygen, the $^3n\pi^*$ character may contribute something to the low quantum yield of the singlet oxygen generation by Mexoryl SX.

The lifetime and ZFS parameters of the T_1 state of 4-MBC, a closely related molecule, were reported previously and listed in Table 2. The anisotropy in the $S_1 \rightarrow T_1$ ISC rates of 4-MBC is also listed in Table 2 [13]. As can be seen in Table 2, the D and D^* values of Mexoryl SX are smaller than those of 4-MBC, suggesting that the two unpaired electrons of Mexoryl SX do not localize on the 4-MBC component in the T_1 state. The T_1 state of 4-MBC is phosphorescent and its lifetime is 17 ms in ethanol at 77 K, while the T_1 lifetime of nonphosphorescent Mexoryl SX is shorter than 10 ms. The delocalized character of the unpaired electrons of Mexoryl SX may be related to its nonphosphorescent character and short T_1 lifetime. On the other hand, the observed anisotropy in the $S_1 \rightarrow T_1$ ISC rates of Mexoryl SX is similar to that of 4-MBC. This fact may suggest that the C=O direction of one 4-MBC component is parallel to that of another 4-MBC component in the T_1 state, as shown in Scheme 1.

4. Conclusions

The Φ_Δ value for Mexoryl SX was determined to be 0.0021 $\pm$ 0.0005 through the measurements of time-resolved near-IR phosphorescence in oxygen-saturated phosphate buffer (pH 7.4) at room temperature. The ability of Mexoryl SX as a photosensitizer for singlet oxygen generation is quite low. The results of the EPR studies showed that the T_1 state is a $^3n\pi^* - ^3\pi\pi^*$ mixing state in character. Although the shorter T_1 lifetime prevents T_1 state quenching by ground-state oxygen, the mixing of $^3n\pi^*$ character into the $^3\pi\pi^*$ state may contribute something to the low quantum yield of the singlet oxygen generation. An ideal UV absorber in cosmetic sunscreens should be photostable and nontoxic without generating singlet oxygen. The elucidation of the T_1 state plays an important role in formulating an ideal UV absorber.

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