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On the photo-oxidation of Perylene bisimide dyes in alcoholic solutions.

Johan Lub[a,b,*], Paul A. van Hal[a,c], Roel Smits[a,d], Lise Malassenet[a,e], Jeroen Pikkemaat[f,g] and Rifat A.M. Hikmet[a,c].

Abstract.

Irradiation with intense blue LED light of Lumogen Orange 240 (**1**) in non-reactive solvents led to bleaching. The products of these photochemical reactions were not possible to determine. Contrarily, irradiation in ethanol or propanol led to red color shifts caused by the formation of the ethoxy or propoxy derivative of Lumogen Orange 240, respectively. These new reaction products of are only formed when both light and oxygen are present. A possible mechanism for these photo-oxidation reactions, the implication for the stability of perylene type of fluorescent dyes under LED lamp conditions and possible preparative applications are discussed.

Keywords

Lumogen Orange 240

Photo stability

Photo substitution

Photo-oxidation

Fluorescent compounds

1   Introduction.

White LED lamps are made with a layer of color converting dyes on top of the blue LED chip, either directly on the chip or in the more efficient remote phosphor configuration [1,2]. In the latter case the more efficient electrical power to light conversion is due to the fact that reflected waves are not absorbed by the LED chip but are able to leave the lighting device without optical losses and thermal quenching. In the remote phosphor configuration more phosphor is needed as a result of the increased surface of the color converting layer [3].

[a] Philips Research, High Tech Campus 34, 5656 AE Eindhoven, The Netherlands
[b] Present address: Eindhoven University of Technology, P.O. Box 513, 5600 MB, Eindhoven, The Netherlands. * Corresponding author j.lub@tue.nl.
[c] Present address Signify, High Tech Campus 7, 5656 AE Eindhoven, The Netherlands
[d] Present address: BDO, Dr. Holtroplaan 15, 5652 XR Eindhoven, The Netherlands.
[e] Present address: Université de Bordeaux, 351 cours de la liberation 33405 Talence , France.
[f] Philips Innovation Services, High Tech Campus 11, 5656 AE Eindhoven, The Netherlands
[g] Present address: Janssen Pharmaceutica, Turnhoutseweg 30, B-2340 Beerse, Belgium.

Inorganic phosphors as the color converter materials are not always preferred due to their price especially in the case of the remote phosphor configuration. Organic phosphors, including derivatives of perylene bisimide, can be a cheap solution for this problem if it wasn't for their relative low stability in comparison to their inorganic counterparts. Several red emitting derivatives of perylene with high quantum efficiency and good photochemical stability can be used for LED lamps [4]. However, the lifetimes of commercially available yellow dyes derived from perylene, that have high quantum efficiencies are much too low for these lighting applications [2,5]. Insufficient photochemical stability of these dyes leads to to early bleaching. For that reason, new yellow emitting dyes were developed that show better lifetimes with preservation of a high quantum efficiency [2,5 6,7]. In order to get more insight in the chemical processes that play a role in the reduced photochemical stability of the perylene derivatives, a study was started to find out which chemical products are formed under intense blue LED irradiation. As a model compound derivative **1** is used. This compound with a bisimide perylene core is an orange emissive dye and serves well as a model compound for this photochemical degradation study. The symmetry of the chemical structure of **1** will be very helpful in interpretation of analytical (especially NMR) data of possible reaction products. Although these dyes are applied in polymer films, the study must be performed in solution in order to be able to separate the photo-reaction products needed for chemical analyses. The photo-degradation of **1** has been studied in polymethyl methacrylate [8,9,10,11] and in solvents [12,13] without analyzing products formed from **1**. Here, the photo-degradation of **1** in solution is studied by attempting to separate its photo-reaction products.

2   Experimental procedure.

2.1   Materials

2,9-bis(2,6-diisopropylphenyl)anthra-[2,1,9-def:6,5,10-d'e'f']diisoquinoline-

1,3,8,10(2H,9H)tetraone (**1**, commercial number: **F240**) was a kind gift from Dr. M.

Koenemann of BASF. All other chemicals and solvents were obtained from Sigma-Aldrich.

2.2   Equipment

For irradiation a homebuilt lighting device with 12 blue LEDs (450 nm) was used, driven at 48V and 0.9 A, yielding a light intensity of ca 4W/cm^2 at a distance of 12 mm. 6 ml samples with a concentration of about 0.2 mmole L^{-1} were irradiated for 4 hours in a glass tube with diameter 25 mm and provided with a magnetic stirrer. The anaerobic experiments were performed with tubes that underwent three freeze-thaw cycles before irradiation. The tubes

were thermostatted in a water bath at 70°C to avoid uncontrolled heating by the LED device. The distance from the vessel wall to the lamp was 12 mm.

Absorption spectra were measured on a Perkin Elmer Lambda 950 UV/Vis spectrometer. Spectra were recorded after dilution of the samples to a concentration of 0.007 mmol L^{-1}. Luminescence spectra were performed on 0.001 mmol L^{-1} ethyl acetate solutions with a Perkin-Elmer LS55 fluorescence spectrometer. The emission spectra were measured by excitation at λ(max) of the corresponding excitation spectrum and the excitation spectra were measured by detecting the intensity at λ(max) of the corresponding emission spectrum. LC-MS experiments were performed on an Agilent 1200 series Liquid Chromatography system fitted with a, 2.1mm ID x 100mm l x 3.5μm dp Eclipse plus C18 column (Agilent). Optical detection was performed using diode array detection and mass spectra were acquired with an Agilent 6210 series TOF-MS using Electrospray Ionisation (ESI) in the positive mode. Preparative LC was performed on a similar system, equipped with a 21.2 mm IDx150mm l * 5μm dp prep-C18 Zorbax column (Agilent) and a diode array detector.

^{1}H and ^{13}C NMR spectra were measured on samples dissolved in deuterated chloroform using Bruker Avance 300 MHz and 600 MHz NMR spectrometers. All chemical shifts were calibrated relative to TMS, δ=0.0 ppm.

Two-dimensional (2D) ^{1}H-^{13}C gradient-enhanced HMBC NMR spectra were acquired at 600 MHz using the "hmbcgplpndqf" pulse sequence available in the Bruker TOPSPIN 2.1 pulse-sequence library [14,15,16]. Evolution periods were optimized for the observation of ^{2}J$_{(CH)}$ and ^{3}J$_{(CH)}$ coupling constants with a value of approximately 8 Hz. Cross peaks originating from ^{1}J$_{(CH)}$ coupling constants were adequately suppressed with the use of a low-pass J filter. No ^{13}C decoupling was used during ^{1}H signal acquisition. As a consequence, residual ^{1}J$_{(CH)}$ cross peaks could be distinguished from ^{2}J$_{(CH)}$ and ^{3}J$_{(CH)}$ cross peaks by the typical splitting of approximately 145 Hz in the ^{1}H dimension.

Spectral properties of 2,9-bis(2,6-diisopropylphenyl)-5-ethoxyanthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetraone (**2a**): ^{1}H-NMR (300 MHz, δ in ppm, J in Hz): = 9.79 (d, J=8.3, 1H), 8.81 (d, J=8.0, 1H), 8.80 (d, J=8.3 1H), 8.79 (d, J=8.1, 1H), 8.75 (d, J=8.2, 1H), 8.71 (d, J=7.9, 1H), 8.59 (s, 1H), 7.53 (t, J=7.5, 1H), 7.52 (t, J=7.5, 1H), 7.38 (d, J=7.5, 2H), 7.37 (d, J=7.5, 2H), 4.68 (q, J=6.9, 2H), 2.77 (m, J=7.1, 2H), 2.76 (m, J=7.0, 2H), 1.77 (t, J=6.9, 3H), 1.20 (d, J=7.0, 24H). ^{13}C-NMR (75 MHz, δ in ppm, *: CH, CH$_2$ or CH$_3$): 163.83, 163.65, 163.62, 163.29, 157.97, 145.59, 145.57, 139.19, 135.21, 135.10, 134.52, 132.53*, 131.35*, 130.59, 130.39, 129.79, 129.72*, 129.63*, 129.54*, 128.85, 128.70*, 127.46, 124.91, 124.12*, 124.10*, 123.84*, 122.89, 122,76, 122.23*, 121.69, 121.09, 119.22*, 66.49*, 29.70*, 24.00*, 14.14*. M + H = 755.35. UV-Vis: λ$_{max}$ (ethyl acetate) = 551

nm, ε = 91500 L mol^{-1} cm^{-1} and 526 nm ε = 67000 L mol^{-1} cm^{-1}. Photoluminescence: λ_{max} (ethyl acetate) = 568 nm.

3   Results and discussion.

Solutions of **1** in benzene or ethyl acetate were irradiated at 70°C for 4 hours. Bleaching of the dye was observed. UV Vis measurements of the solutions during and after irradiation did not give other spectral information than a decrease of the absorption of about 10%. LC-MS experiments with these samples didn't show any new compounds that absorb in the visible region or showed separate peaks in the UV region with well-defined mass. Thus, no conclusion could be obtained of the products that could be formed due to the irradiation. Probably, the degradation products were instable and did not contribute to the absorption spectrum.

If the same irradiation experiments with **1** were performed in ethanol or n-propanol, the characteristic yellow/orange color of the dye changes to pale red. Formation of a red colored compound after irradiation is also apparent from the absorption spectrum of such a solution; a new peak at 551 nm arises during irradiation as depicted in Figure 3-1.
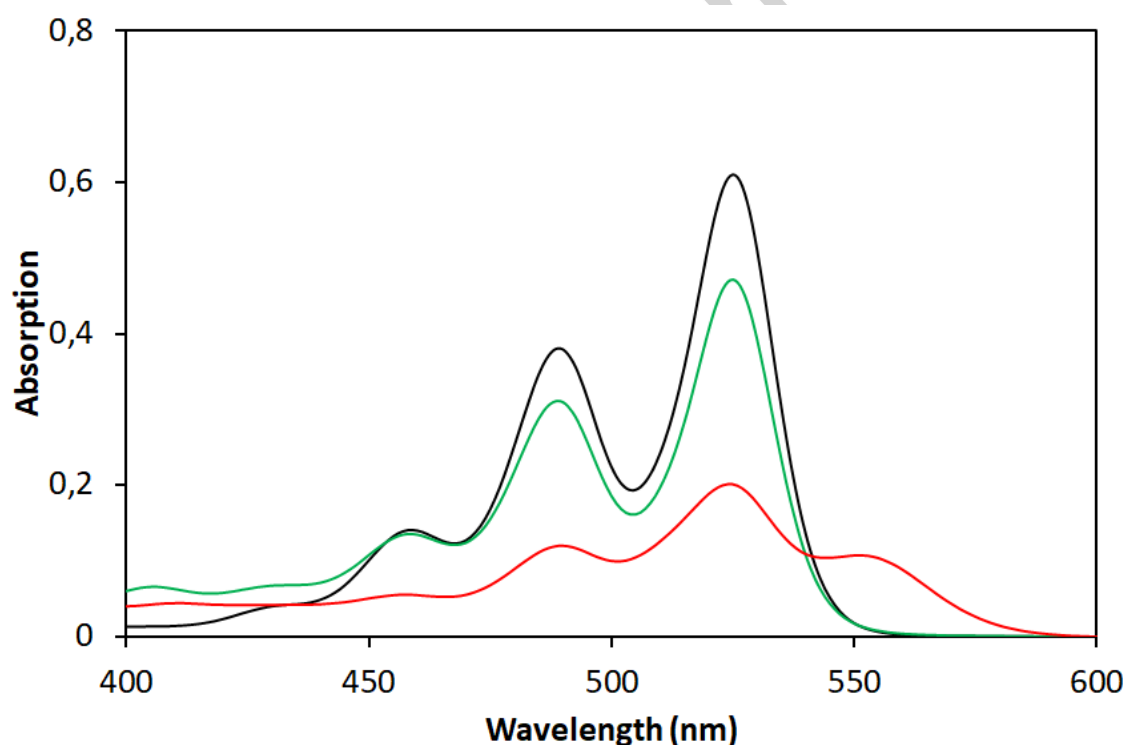

Figure 3-1   UV-Vis spectrum of **1** in ethanol before irradiation (black curve), after 4 hours of irradiation under vacuum (green curve) and after 4 hours of irradiation under aerobic conditions (red curve) in ethanol.

Irradiation of the same sample under vacuum instead of air resulted in a slower decrease of the original spectrum and without formation of the new 551 nm peak, see also Figure 3-1. Furthermore, an ethanolic solution of dye **1** kept at 70°C for 4 hours didn't show any change in the spectra or in LC-MS traces, when the dye was not illuminated. Thus, for the transformation in ethanol, both oxygen and light are needed. Interestingly, LC-MS experiments revealed that the transformation in n-propanol results in a new compound with a mass 14 amu higher than the product formed in ethanol. This leads to the conclusion that the alcohols are incorporated in the dye during the reaction. The absolute values of the mass of the newly formed compounds is 2 amu less than the sum of the mass of compound **1** and one of the alcohols which points to a photo-oxidation reaction.

With the aid of preparative LC-MS the newly formed compounds were isolated. Figure 3-2 shows the photoluminescence spectra in ethyl acetate of the starting compound **1** and the isolated product obtained after the photo-oxidation reaction in ethanol. The excitation spectra exhibited the same shape as the absorption spectra in ethyl acetate. The compound obtained in n-propanol exhibits the same spectra as the compound obtained in ethanol. The red color of the new compounds can be attributed to a substitution of one of the hydrogens in compound **1** by an ethoxy or propoxy group originating from ethanol or n-propanol, respectively. Reaction occurred with the oxygen atom of the alcohol as concluded from the ^{1}H-NMR spectra of the product of the reaction product with ethanol that exhibit signals at 4.68 ppm (quartet, J=6.9Hz) and 1.77 ppm (triplet, J=6.9Hz) and of the product with n-propanol at 4.58 ppm (triplet, J=6.4Hz), 2.17 ppm (multiplet) and 0.88 ppm (triplet, J=6.8Hz).

The color change observed by the reaction with the alcohols point to a reaction of the alcohol with the perylene moiety. Various derivatives of **1** are known with **H**[b] (see Figure 3-3) substituted by oxygen, that are red, and exhibit absorption peaks around 550 nm [17,18]. Thus, structure **2a** is an obvious candidate as reaction product.

Further ^{1}H-NMR analysis of the photo-oxidation product with ethanol reveals that the two characteristic doublets of **H**[a] and **H**[b] of the starting product (see Figure 3-3) are split into 6 doublets and one singlet (see horizontal trace of Figure 3-4). This spectral change can be explained by the substitution of one of the protons **H**[a] or **H**[b] by an ethanolate group and the concomitant loss of the four-fold symmetry of the starting product. The singlet can be attributed to **H**[c] or **H**[d] in the case of **2a** or **3a**, as possible structures, respectively. To distinguish between structures **2a** and **3a**, an NMR 2D C-H 3 bands coupling spectrum was recorded (see Figure 3-4). Coupling of the carbonyl carbons of the imide groups that exhibit signals around 165 ppm is only possible with **H**[c] (3 bands coupling) and not with **H**[d] (4 bands

coupling). From the relatively intense cross peak between the proton singlet signal at 8.59 ppm and one of the four carbonyl carbon signals of the imide groups it can be concluded that the reaction product corresponds to structure **2a**. The product obtained after irradiation in 1-propanol exhibits nearly the same spectral properties in the aromatic region and has therefore structure **2b**. The position of the substituent in the perylene ring, namely the carbon atom with **H**[b] is not completely surprising. The reactivity of these positions in the perylene ring is known to be the highest [19].

Absorption of both compounds **1** and **2a**, measured with the spectral detector of the LC-MS and the NMR spectra of the crude mixtures reveal a conversion of about 30%, before notable byproducts formation occurs. This is mainly observed as bleaching similar to the bleaching in not reactive solvents such as ethyl acetate. No prove for products with more substitutions by ethanol were found. Probably **2a** exhibits a relative good stability towards photo-oxidation. This points to a possible reparative method to make photochemically derivatives of **2a** with selected alcohols instead of ethanol. This will be investigated in a forthcoming study.
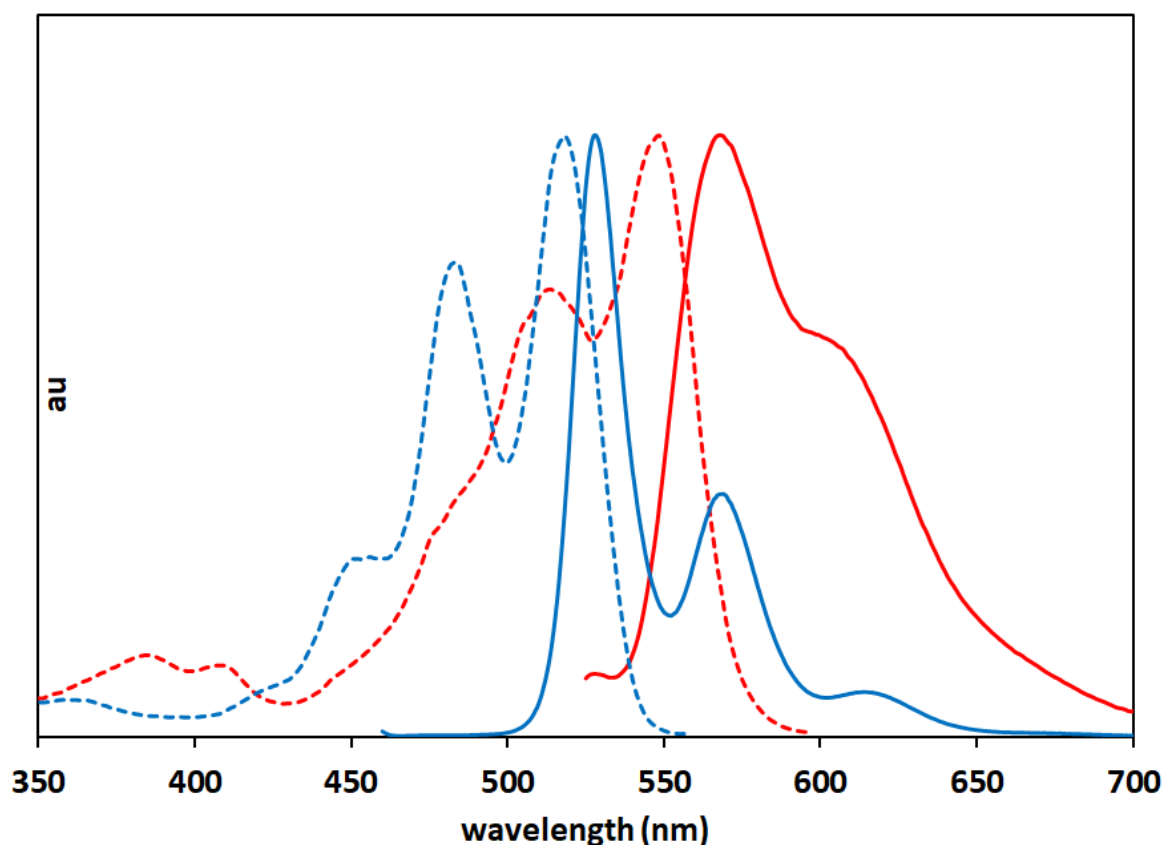

Figure 3-2 *Photoluminescence spectra of **1** (blue) and **2a** (red) in ethyl acetate. Dotted lines represent excitation spectra and uninterrupted solid lines represent emission spectra.*
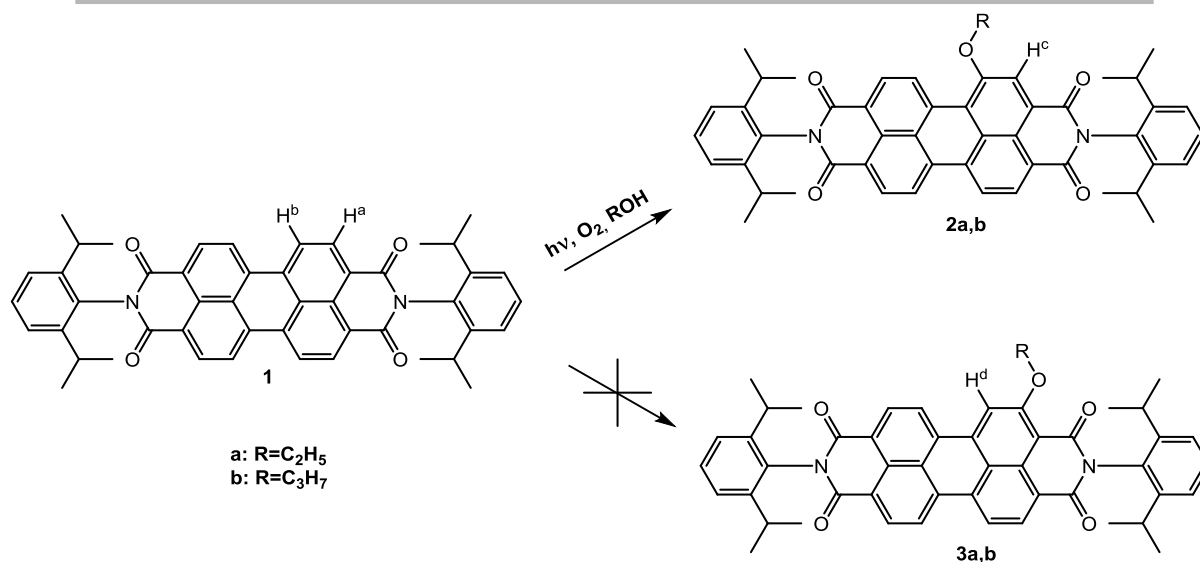
Figure 3-3 Formation of **2a** and **2b** by reaction of **1** with ethanol and n-propanol, respectively. Compounds **3a** and **3b** are possible isomers of **2a** and **2b**, respectively, as discussed in the text.
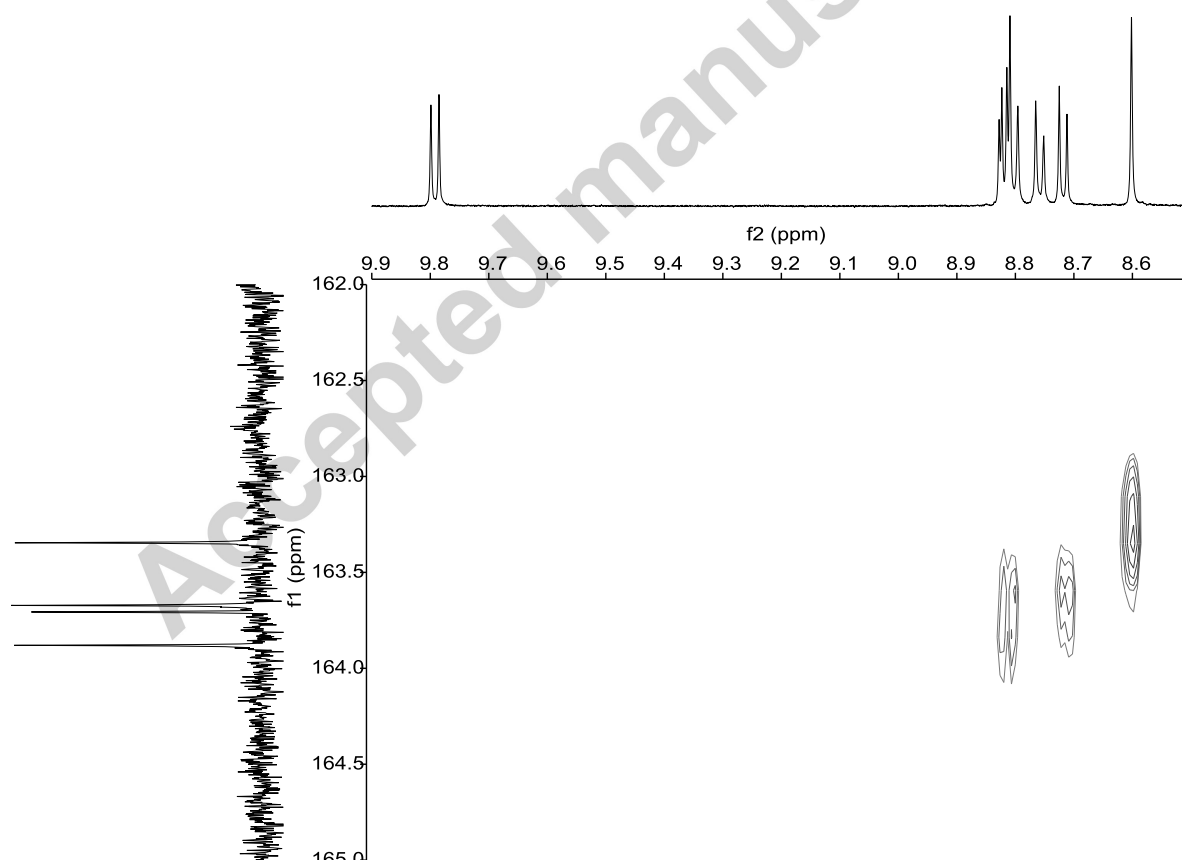

Figure 3-4 Part of the 2D ^{1}H-^{13}C HMBC spectrum in deuterated chloroform of the reaction product of **1** with ethanol.

The negative effect of oxygen on the photo-stability of **1** and other perylene derivatives in polymeric materials was already shown in former studies. Although, these studies determined kinetics and spectral changes instead of real products as a result of the photo-degradation processes it was concluded that the photo-degradation is mainly caused by photo-oxidation processes [4,8,20]. The fact that irradiation under aerobic conditions leads to a much faster degradation in mentioned studies, and the fact that reaction with the alcohols occurs only in the presence of oxygen point to a process in which oxidation of **1** is the first step to obtain a reactive species that reacts with the alcohol. Such a mechanism is outlined in Figure 3-5.
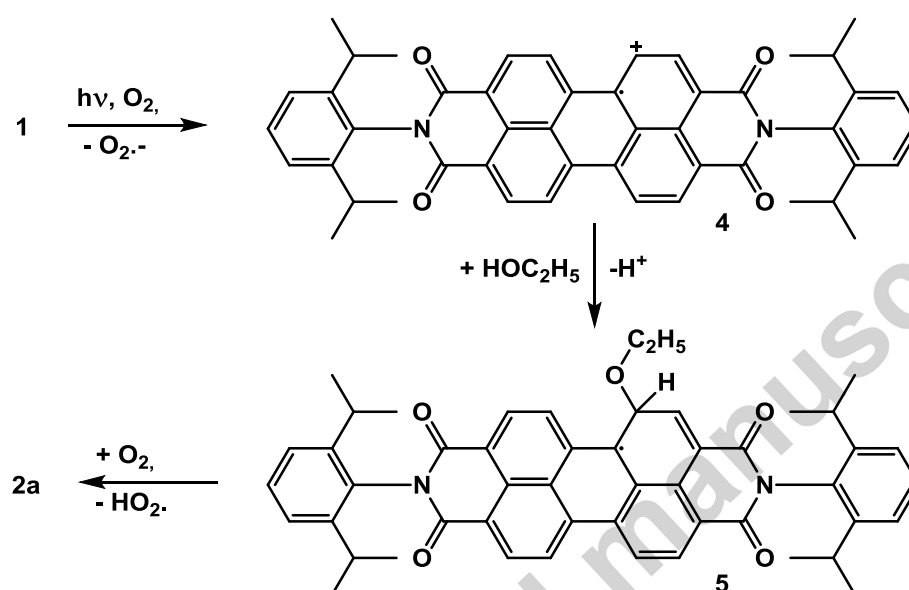

Figure 3-5 Proposed mechanism for the oxidative addition of ethanol to **1** during irradiation with 450 nm light.

The nature of the oxygen species formed is not clear. Stoichiometrically half an oxygen molecule is consumed in the reaction. Although formation of singlet oxygen can be expected from these type of dyes [9], other studies indicate that in the case of **1** oxidation with the formation of superoxide or hydroperoxide is more likely [12]. Photo-ionization of **1** has been proposed which leads to fast bleaching in oxygen [21], which may prove the formation of **4** in air. The reaction of radical cation **4** with the nucleophilic ethanol is rather obvious and it is expected that other less nucleophilic solvents such as ethyl acetate and benzene are not incorporated, which explains the absence of formation of perylene derived reaction products similar to **2a**. The suggested formation of superoxide (O_2^-) in the transformation of **1** into the radical cation **4** (see Figure 3-5) may also lead to reduced **1** (radical anion) [22]. The oxidation as well as reduction of these perylene derivatives are considered as reactions ultimately leading to bleaching of these compound under photo-oxidation conditions

[12,22,10]. However, chemical evidence of the intermediates that play a role in the finally bleached products have not been described. It is very likely that the oxidized intermediate **4** is trapped by the nucleophilic ethanol and that reaction with superoxide doesn't occur under these conditions due to the protonation of superoxide by the solvent or by the proton generated upon reaction of **4** with ethanol.

4   Conclusions.

The photo bleaching of Lumogen Orange 240(**1**) was investigated as a model compound for photo luminescent colour conversion in LED by perylene derivatives. This bleaching starts probably with the photo-oxidation to reactive radical cation **4** which ultimately leads to formation of non-colored species in a sequence of reaction. Unfortunately, it was not possible to detect any of the reaction products. In ethanolic solution the reactive intermediate **4** seems to be captured with the formation of ethoxy derivative **2a**. The relatively good conversion to **2a** points to a good stability of **2a** towards the photo-oxidation conditions. This might be explained by the fact that this compound is less reactive under these reaction conditions; the ethoxy groups lowers the ionization potential and/or by the fact that after oxidation of **2a** a relatively more stabilized radical cation is formed that restrains further reactions other than reduction by the initially formed superoxide. The use of this photo-oxidation reaction for preparative purposes and the stability of alkoxy-stabilized derivatives of **1** will be topics of forthcoming studies.

Acknowledgements

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