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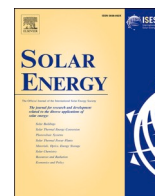
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Initiation and recovery of damage initiated by UV irradiation in luminescent solar concentrators deposited in ambient conditions

Pam Berghuis^{a,b}, Frankjen Y. de Boer^b, Jeroen ter Schiphorst^b, Michael G. Debije^{a,c,*}

^a Stimuli-responsive Functional Materials and Devices (SFD), Department of Chemical Engineering and Chemistry, Eindhoven University of Technology (TU/e), Groene Loper 3, 5612 AE Eindhoven, The Netherlands

^b Lusoco B.V., 5612 AP Eindhoven, The Netherlands

^c Eindhoven Institute of Renewable Energy Systems (EIRES), Eindhoven University of Technology, PO Box 513, Eindhoven 5600 MB, The Netherlands

ABSTRACT

Photopolymerization of thin, dye-doped acrylate-based layers under ambient conditions often requires high concentrations of photoinitiators. The radical storm created during polymerization has been shown to cause damage to the embedded fluorescent dyes; some of this damage is repaired upon exposure to air, but a fraction of the damaged molecules do not repair. This work presents a more detailed optical study of the environmental effects, nature of the initiator, and resulting fluorescence of the dye molecules caused by photopolymerization, all factors necessary to understand and control to allow ambient inkjet printing of these luminescent species.

1. Introduction

A luminescent solar concentrator (LSC) is a device for collecting, downshifting, distributing, and concentrating sunlight for use in the urban setting to produce electricity [1–5], fine chemicals [6], hydrogen [7], or for a variety of other potential uses [8–13]. The LSC generally consists of a glass or polymer lightguide doped with a fluorescent material. Incident sunlight is absorbed by the luminophore and emitted at a longer wavelength, a fraction of this light becoming trapped by total internal reflection in the lightguide, exiting only through the edge(s) of the device. LSCs can be produced in different shapes [14,15], can be made in different colors [16,17], and work both in direct and indirect light [18].

Another way to produce the LSC device is by applying the luminescent material as a thin layer on top of a transparent lightguide made of glass or polymers, like PMMA or (poly)carbonate [19]. Our own interest lies in depositing the luminescent material via inkjet printing [20], and simplifying industrial production by polymerizing the dye layer in ambient conditions; that is, avoiding the necessity of a nitrogen atmosphere. It has been previously shown that care must be taken in this procedure, as the exposure to the radical storm of polymerization can lead to reduction of the luminescent species [21,22].

In this work, the focus is on a common organic luminophore used in LSC devices based on a perylene core, the commercial red fluorescent dye Lumogen F Red305 [23], the workhorse of LSC research due to its

high fluorescent quantum yield [24] and extended photostability [25]. A common commercial technique to photopolymerize inkjet inks under ambient conditions is significantly increasing the photoinitiator (PI) concentration to mitigate oxygen inhibition of the photopolymerization. However, increasing PI concentration results in the appearance of additional absorption peaks when the inks are exposed to intense UV in nitrogen atmosphere [22,26] which may significantly reduce edge emissions from the device. The additional absorbance peaks disappear after exposure to air, indicating the presence of an unstable radical anion being formed during the UV light exposure. Expanding on our previous work [21], a systematic optical study is performed, providing a more detailed study of the formation of the radicals in the context of an LSC application, identifying the source of the radical damage, and the influence of external factors such as heat and oxygen. By understanding these mechanisms, guidelines for alterations in the ink composition and/or polymerizing conditions can be made to enable atmospheric inkjet printed LSC devices.

2. Experimental

The standard ink composition containing thiols and acrylates, *Ink1*, was kindly provided by Lusoco. To this base material, the dye N,N-bis(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxy-3,4,9,10-perylenetetra-carboxylic diimide (Red305, BASF), and various photoinitiators (PIs): diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO),

* Corresponding author.

E-mail address: m.g.debije@tue.nl (M.G. Debije).

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Sigma Aldrich) and one of the PIs phenylbis(2,4,6-trimethylbenzoyl) phosphineoxide (I-819, Sigma Aldrich)), 2-methyl-1-(4-(methylthio) phenyl)-2-morpholinopropam-1-one (I-907, Ciba), 1-([1,1'-biphenyl]-4-yl)-2-methyl-2-morpholinopropan-1-one (I-307, Ciba), 1-hydroxycyclohexyl phenyl ketone (I-184, Ciba), or azobisisobutyronitrile (AIBN, Aldrich) are added at various concentrations. The ink formulations are listed in Table 1. Initiator concentrations were chosen in range of commercial inkjet printing inks, often between 5 and 15 wt% in total concentration (from private consultation with printing firms).

The components were magnetically stirred overnight at 400 rpm at room temperature. If undissolved parts were observed, ink mixtures were heated at 40 °C for several hours while stirring, with additional sonication of the ink mixture for \pm 30 min if incomplete dissolution was suspected.

3x3 cm² glass cells were made using Norland UV 91 glue containing 20 μ m spacers and filled with ink by capillary action. For drop casting, clean 3x3 cm² glass plates were treated in the UV-ozone oven for 20 min, and 100 μ L of the ink mixture was deposited using an Eppendorf pipette (impact of deposition and layer thickness of quantum yields are found in Fig. S1). The ink was spread evenly over the entire surface of the glass plate with the pipette tip. Both the glass cells and drop casts were photopolymerized using the Aktiprint 12–1 UV dryer (AKP) equipped with a high-power halogen (HP Hg) lamp, generally by passing the sample 10 times through at a belt speed of 3 m/min, resulting in a total dose of 8.5 J/cm² unless otherwise noted. Photopolymerization of samples in nitrogen environments was performed using an EXFO Omnicure S2000 lamp with a 320 – 500 nm filter at 8.5 J/cm² (unless noted). When needed, opening of the glass cells was done by carefully sticking a razor blade between the two glass slides.

Fluorescence quantum yield (FQY) measurements were performed using a Labsphere LMS-100 integrating sphere. The sample are irradiated with a 530 nm LED with a collimator to create a narrow beam which resulted in a spot of light of approximately 1 cm in diameter on the sample through a 6 mm diameter pinhole. During measurement, the side of the sample containing the polymerized ink faced the incoming irradiation beam. The quantum yield measurements are performed using a two measurement approach including two dark measurements to correct for any stray light [24]. The entire measurement for the FQY_{eff} consisted of four different scans: 1) No sample, only LED (light measurement); 2) No sample, no LED (dark measurement); 3) Sample and LED (light measurement); 4) Sample, no LED (dark measurement). The FQY_{eff} was calculated from these four scans: for more details see the SI. In the first step, the dark measurements were subtracted from the associated light measurements. This implies the subtraction of scan 2 from scan 1, and scan 4 from scan 3. The number of photons was then plotted against the wavelength and these peaks were integrated. The resulting peak areas of the sample emission (Emiss), and LED peak both in the presence (Sample_LED) and the absence (LED) of the sample were finally used to determine FQY_{eff} (Formula 1).

$$FQY_{eff} = \frac{E_{miss}}{LED - Sample_LED} \quad (1)$$

Additional information can be found in the SI and Fig. S2.

Absorbances were determined using a Lambda 750 UV/Vis/NIR spectrophotometer (PerkinElmer). Solid samples were attached using double-sided tape to the edge of the cuvette holder with the polymerized

ink towards the incoming light beam. Emission and excitation spectra were measured with a FLS900 photoluminescence spectrometer (Edinburgh Instruments) equipped with a visible light detector.

3. Results and discussion

Colorant Red305 has near unity FQY in dilute solution [12,27], and has found extensive use in LSC-type devices because of its long term stability [23]. The relatively high concentration of 1 wt% Red305 used reduces the FQY_{eff} of the ink from reabsorption events due to the dye's limited Stokes shift. As a control experiment, the unpolymerized *Ink1* was introduced inside a glass cell, and a FQY_{eff} of 83% was determined.

A drop cast sample of *Ink1* was also measured. To overcome the scavenging of initiated radicals by oxygen, a significant excess of PI (10.5 wt%) and high light dose are needed in ambient conditions, resulting in a FQY_{eff} of only 9% immediately after photopolymerization, coinciding with a dramatic color change from red to burgundy (see Fig. 1a–c). After five days in ambient conditions, the FQY_{eff} partly recovered to < 40%, and the color changed back to red. This 'recovery' of FQY_{eff} and color was accompanied by an apparent increase in edge emission. The absorption spectra of another sample using *Ink1* ink before and after photopolymerization using the AKP are shown in Fig. 1d–e. The decrease in absorbance below 400 nm is the result of conversion of PI I-819 and TPO upon radical formation [28].

Five additional absorption peaks between 650 and 1200 nm appear immediately after polymerization, and the FQY_{eff} in this sample drops from 83 to 18%. The absorption peaks of the peaks at 790, 980 and 1085 nm are related to a nonfluorescent radical anion, and the peaks at 670 and 711 nm to a fluorescent dianion with a FQY of 17%, in the medium similar to that described earlier [20], relative to the neutral Red305 species, at 738 nm [22,26].

Emission spectra are recorded: Fig. 2a shows the emission spectra upon excitation with 575 nm before and after photopolymerization, the peak-absorbance of Red305 [12,27]. The emission spectra show both the main and the second emission peak of the Red305 molecules at approximately 600 nm and 650 nm, respectively. After photopolymerization of the ink, there is an obvious decrease in emission from the Red305 molecules, most likely due to a generation of non-emissive products. Fig. 2b shows the emission spectra before and after photopolymerization upon excitation with 670 nm, a wavelength where the dianion absorbs. Before polymerization, there is no obvious emission in the range 680–800 nm. After polymerization, however, a significant increase in emission in the wavelength range coinciding with the dianion [22] is seen.

The permanent reduction of the absorbance results in a significant, permanent loss in final FQY_{eff}. The absorption spectra of the *Ink1* were measured inside a glass cell, and the resulting spectra together with the measured FQY_{eff} are shown in Fig. 1d. The source of this permanent drop in FQY_{eff} is not easily explained. Even though there is partial recovery of performance and the near-complete loss of measurable anionic species, apparently there remains neutral damage species we are not able to easily detect, degradation products that might quench the FQY_{eff} of the sample: [22] only a small presence of quencher can have a significant effect on the FQY_{eff} [29]. It has also been shown even a very minor absorbance can have dramatic impact on edge emissions in LSC devices [30].

To follow recovery, the absorption spectrum of a drop cast film containing *Ink2* (similar to *Ink1*, but with less dye) was followed over 34 h in ambient conditions. The resulting spectra are given in Fig. 3. There are clear decreases in absorption for both the radical anion and the dianion species over time. Simultaneously, there is a corresponding recovery in the absorption corresponding to the Red305 molecules.

The reported molar extinction coefficients of the different species (Table S1) were used to calculate the relative concentrations of the radical species (Fig. 3c) under the assumption that these values are similar when used in this ink matrix [22]. Most of the reversion of both

Table 1

Initiator and dye composition of the standard inks: the remaining fraction consists of the acrylates and thiol-acrylates.

| | Concentration (wt%) | | | |
|--------|---------------------|-------------|-------------|-------------|
| | <i>Ink1</i> | <i>Ink2</i> | <i>Ink3</i> | <i>Ink4</i> |
| TPO | 7.5 | 7.5 | 7.5 | 0.7 |
| I-819 | 3.0 | 3.0 | 3.0 | 0.3 |
| Red305 | 1.0 | 0.25 | 0.125 | 1 |

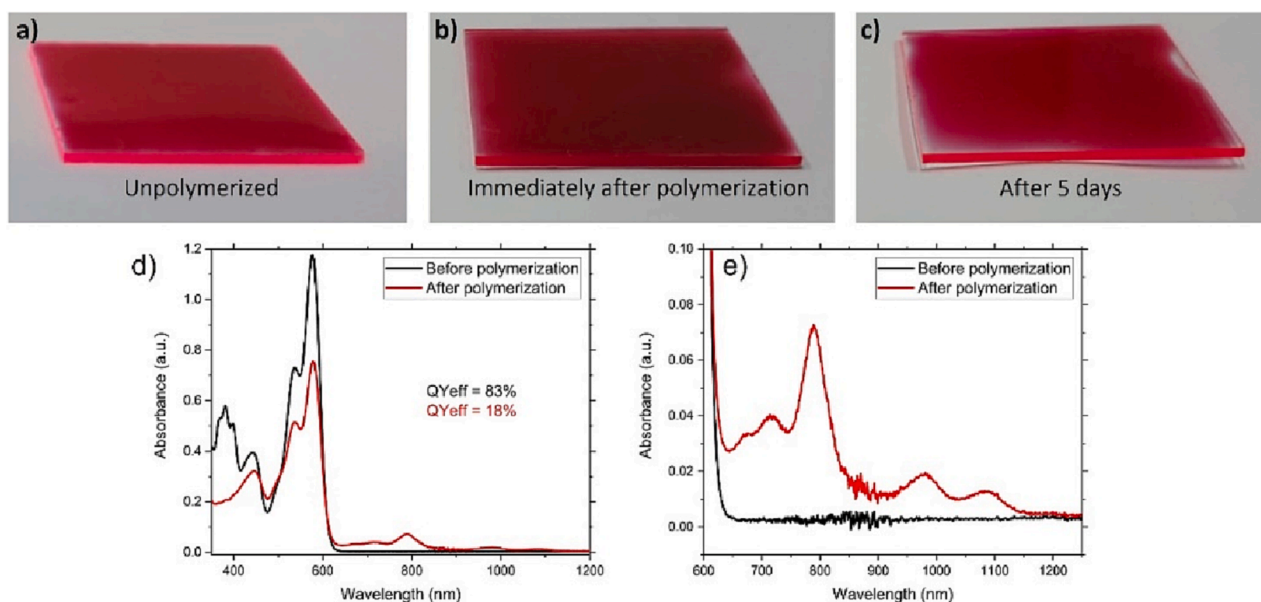


Fig. 1. Representative photographs of a) unpolymerized drop casts of *Ink1*, b) immediately after polymerization and c) polymerized ink after 5 days in an ambient environment. The pictures clearly show the difference in color and edge emission upon photopolymerization and ‘recovery’. d) Absorption spectrum of a sample using *Ink1* before (black line) and after (red line) photopolymerization with the AKP inside a glass cell showing the additional absorption after polymerization and the decrease in absorbance of the Red305 molecules. The FQY_{eff} of the two states is also shown. e) Zoomed in absorption spectrum, showing the five additional absorption peaks after polymerization.

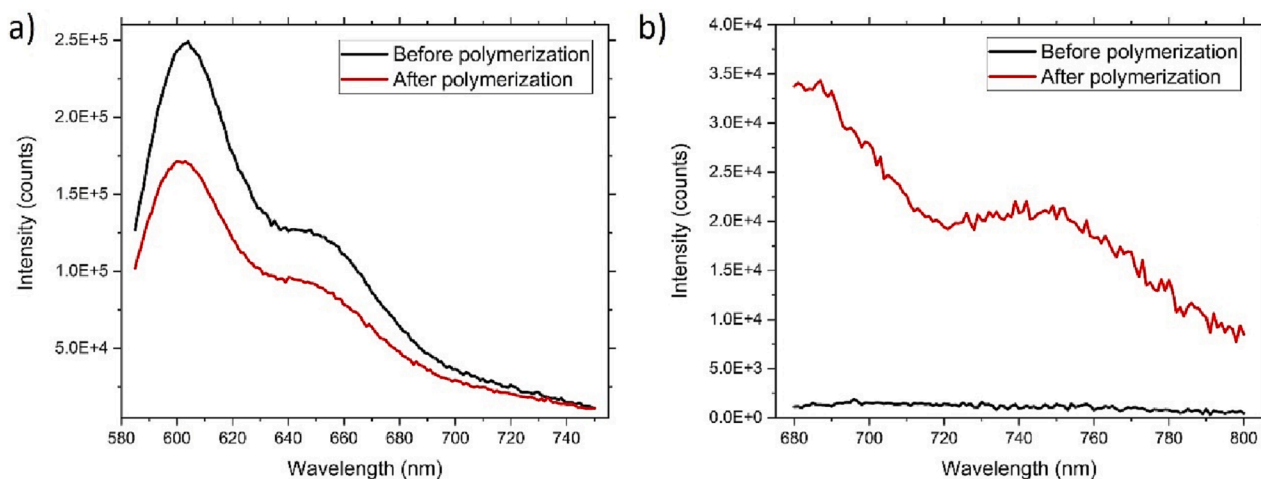


Fig. 2. Emission spectra of a glass cell with the *Ink3* ink before and after photopolymerization with the AKP upon excitation with a) 575 nm and b) 670 nm.

reduced species as well as the recovery of the Red305 molecules occur within the first 12 h, with the more abundant radical anion reverting significantly faster than the dianion, suggesting an increased stability of the dianion in the polymerized system.

Scavenging of the reduced species is expected to be more rapid in a thinner polymerized film due to the easier penetration of oxygen [28,31]. For this experiment, ink was first photopolymerized inside a 20 μm glass cell, and the cell opened, allowing oxygen to penetrate the film. The recovery of the dianion of the glass cell is compared to that of the much thicker drop cast films. The absolute decrease is 8 times faster for 20 μm film than for the 150 μm drop cast sample (see Fig. S3).

The influence of oxygen and the possible peroxy-radicals formed on the reduction of Red305 during photopolymerization was evaluated using *Ink2* drop cast samples. The samples were exposed to light from the EXFO, the same total dose used during curing with the AKP. The polymerizations were executed in oxygen and nitrogen environments: the two absorption spectra are essentially identical (see Fig. S4a). A

separate experiment comparing the same degassed ink polymerized under nitrogen showed similar results (see Fig. S4b). The reduction of the Red305 molecules both in the presence as in the absence of oxygen suggests peroxy-radicals, which would be formed upon reaction of the PI radicals with oxygen, are not responsible for reduction of the colorant.

The subsequent scavenging of the radical anions and dianions by oxygen was evaluated. The polymerized samples were kept in either ambient or argon atmospheres, and absorbance spectra taken after sitting overnight. The absorption of the reduced species decreases over time in ambient conditions, consistent with scavenging by oxygen [22,31], while the sample in the argon environment does not show a similar decrease (Fig. S5). The conclusion is oxygen does play a significant role in scavenging of the reduced species.

The influence of temperature on the reversion of the reduced species was tested by heating newly polymerized cell for 90 min at 100 $^{\circ}\text{C}$ and following the recovery of the dianion, and comparing to an open sample under ambient conditions (Fig. S6). In the first 10 min. there is a steep

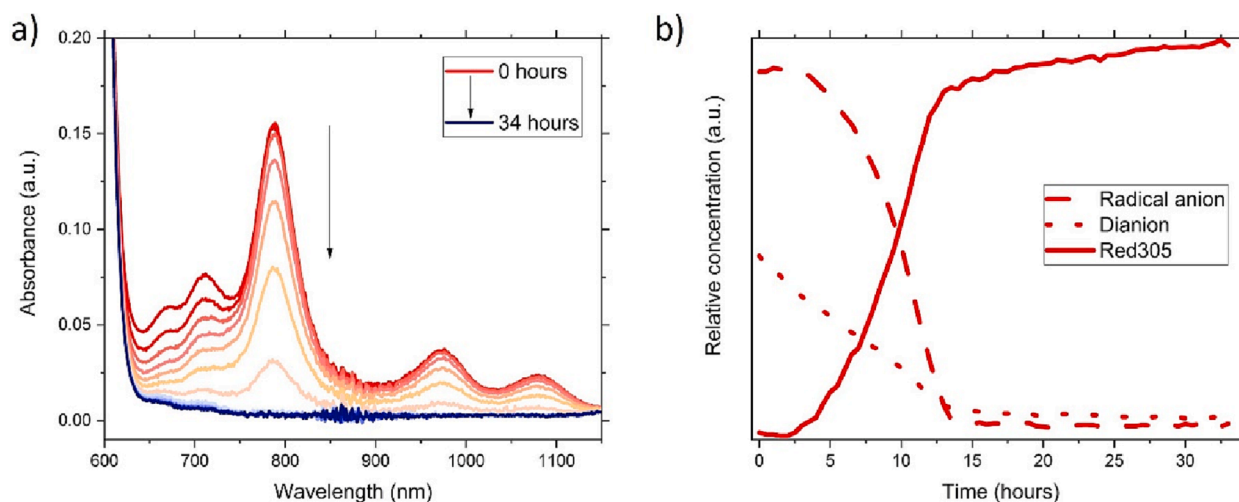


Fig. 3. Time dependent absorption spectra in ambient conditions of a *Ink2* drop cast (layer thickness of $\pm 150 \mu\text{m}$) polymerized with the AKP. a) Decrease in absorbance of the reduced species, and b) the relative concentration of the radical anion, dianion, and Red305 molecules over time during ‘recovery’ of a *Ink2* dropcast in ambient conditions.

decrease of 88% of the dianions in the heated sample. A similar decrease in absorbance under ambient conditions takes more than 10 h. This difference shows a significant influence of heat on the speed of reversion of the reduced species. The increased rate of recovery upon heating in the glass cell could be explained by enhanced mobility of electrons and oxygen inside the polymer upon exceeding of the glass transition temperature [32]. The more rapid recovery of the reduced species in the cell resulted in a final FQY_{eff} of 45%, similar to the 47% after recovery in ambient conditions. The similar FQY_{eff} suggests similar damage and recovery pathways, resulting from either higher oxygen mobility or greater electron mobility.

The formation of the fluorescent dianion and the decrease in the concentration of the Red305 molecules during photopolymerization was probed by the change in emission spectra before and after polymerization of a sample using *Ink3*, similar to *Ink1* and *Ink2* but with lower dye concentration, a sensitive probe for these effects [33]. The transfer of some energy from the Red305 dye to the dianion was verified by measuring excitation spectra before and after polymerization. The sample was excited with 400 nm to 730 nm light, and the corresponding emission at 740 nm, the peak emission of the dianion [22], was monitored. The resulting excitation spectra both on a logarithmic scale before and after polymerization are shown in Fig. S7.

Before polymerization, the excitation spectrum shows no influence from wavelengths greater than 620 nm, as expected for Red305. After photopolymerization, the fluorescent intensity after excitation below 475 nm and between 525 and 600 nm decreases. This decrease coincides with the decrease in absorbance of the Red305 molecules observed upon polymerization. Concurrently, excitation with light of 600–700 nm results in an increase in fluorescence intensity, a consequence of the presence of the dianion molecule after polymerization. Thus, part of the influence of the reduction of the Red305 molecules on the FQY_{eff} is likely related to reabsorption and reemission events; the dianion species absorbs some light emitted by the Red305 molecules, emitting itself only with a FQY of $\sim 17\%$ and the anion does not emit at all [22]. The possible direct energy transfer between the Red305 molecules and the radical anion/dianion molecules was explored by measuring the fluorescence lifetime of the sample before and after photopolymerization (see Fig. S8). To isolate the specific ink component responsible for the reduction of Red305, ink compositions were made where the PIs, thiols and acrylates were individually absent. The absence of components was compensated by adding additional acrylate to the ink mixture. The compositions of the ink formulations are given in Table 2. For the compositions containing no acrylates, the solvent with similar chemical

Table 2

Ink compositions of the modified *Ink1*. The acrylates and thiol-acrylates make up the bulk of the ink.

| | Quantity (wt%) | | | |
|--------|----------------|-----------|-------------|-------------------|
| | No_PI | No_thiols | No_acrylate | No_acrylate_No_PI |
| TPO | 0 | 7.5 | 7.5 | 0 |
| I-819 | 0 | 3.0 | 3.0 | 0 |
| Red305 | 1.0 | 1.0 | 1.0 | 1.0 |

structure to the most abundant acrylate was selected, and assumed to not interfere with the remaining ink components. The inks were illuminated in glass cells using the AKP, the resulting absorbance spectra before and after polymerization as well as a picture showing the color change upon illumination are given in Fig. 4.

The ink containing no PI shows no reduction, maintaining its reddish color after illumination. There is a pronounced reduction and color change seen for ink lacking the thiols. Thiols react with radicals by exchanging their proton, leaving a thiyl radical. A reaction between a thiol and a PI radical can, in this way, ‘soften’ the PI radical, making it unable to reduce Red305. In the absence of thiols this reaction does not occur, and more highly reactive PI radicals remain, resulting in strong reduction of the Red305 molecules.

The ink containing no acrylates shows a severe color bleaching and a blue shift in absorption of the Red305 molecules, indicating direct degradation of the fluorescent dye molecules [34]. Since Red305 is generally considered a stable organic dye [12] this rapid degradation is most likely caused by the direct attack of the dye by the PI radicals which have no acrylates with which to react. This conjecture is supported by illuminating an ink formulation without acrylates and without PI: the Red305 molecules remain intact. Repeated illumination of a sample that had previously recovered but which still contained unused PI resulted in the formation of new anion and dianion species: if unused PI remains in the system, even once fully polymerized, the potential for radical attack persists (see SI Fig. S9).

The effect of altering the concentration of PIs in the ink mixes was examined. An ink with a total of 1 wt% PI (*Ink4*) was photopolymerized inside a glass cell using the AKP. The resulting absorption spectra before and after photopolymerization as well as after ‘recovery’ are compared to the *Ink1* containing 10.5 wt% PI (see Fig. S10).

The Red305 absorption peak of the *Ink4* decreases significantly less when compared to *Ink1* upon photopolymerization: after ‘recovery’, *Ink4* had only 11% loss of absorbance compared to 25% for the *Ink1* ink.

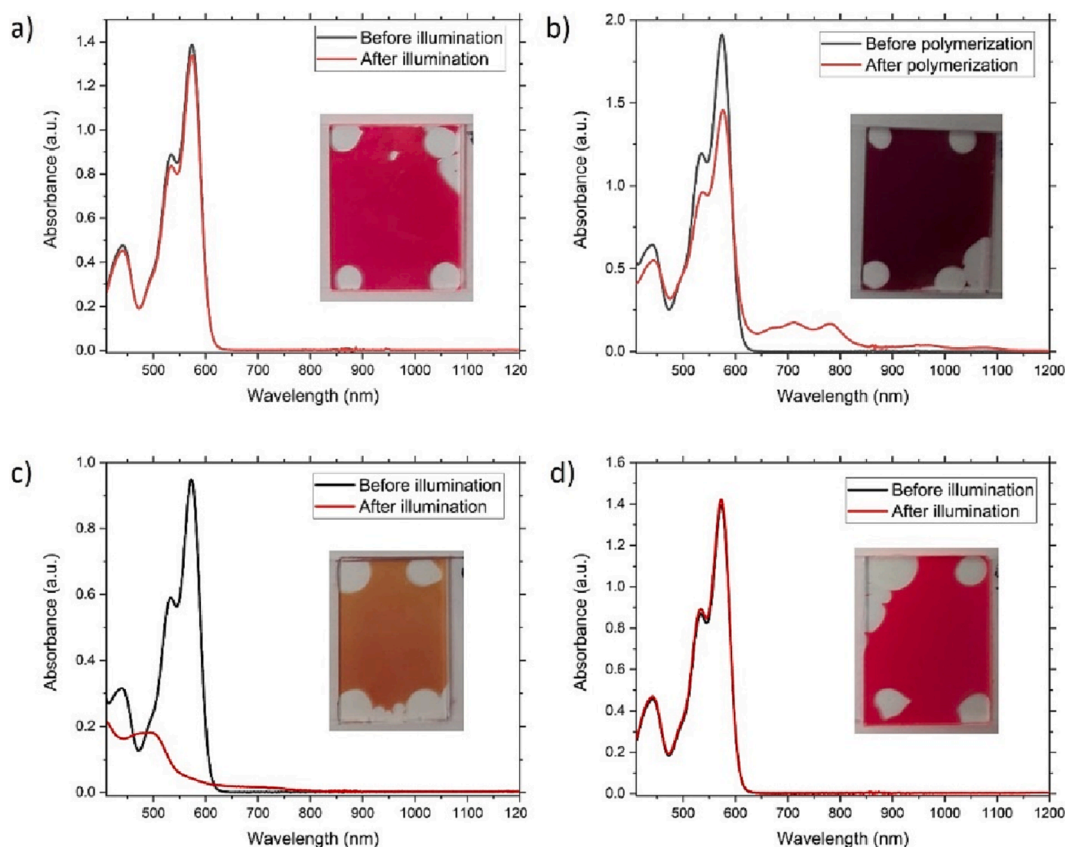


Fig. 4. Absorption spectra before and after light illumination with the AKP (5.95 J/cm^2 for the *No_acrylate* ink) of the respective inks inside a glass cell, as well as a picture showing the resulting color of the ink after this illumination for the a) *No_PI* ink, b) *No_thiols* ink, c) *No_acrylate* ink, and d) *No_acrylate_No_PI* ink.

The main difference between the photopolymerization is the quantity of PI radicals formed. For *Ink1*, radicals are most likely formed after every pass under the AKP, whereas for *Ink4*, the reactions are completed earlier, and in total less PI radicals are formed. The formation of less radicals leaves less radicals to react with the Red305 molecules. Apparently, the radicals that do react with the Red305 molecules primarily reduce these molecules once, forming radical anions. It appears additional PI radicals are necessary to produce dianions from the anions, as is the case for *Ink1*. This observation would be in line with results from literature for the reduction of a comparable dye molecule where it was found that the formation of the dianion goes via the monoanion [35].

Even though more reduced species appear to be formed for *Ink4*, less permanent loss in the absorbance of the Red305 is observed. When assuming the absorbance at 711 nm for the *No_PI* ink to be primarily from the dianion, a similar concentration of the dianion appears to be formed during the photopolymerization of *Ink4*. Since the formation of the dianion is expected to result in enhanced photodegradation [22], resulting in a loss in absorbance of the Red305 molecules, additional mechanisms are expected to occur decreasing the absorbance of the Red305 molecules for *Ink1* even further. Given the considerable difference in PI concentration between *Ink1* and *Ink4*, an additional quencher molecule is possibly formed, perhaps a complex between the PI and the Red305 molecules, possibly helping to explain why, for the *Ink4* ink, after recovery, a FQY_{eff} of 67% was found, whereas for *Ink1* only a FQY_{eff} of 47% remained.

TPO and I-819 were expected to be similar as they both function via α -cleavage of the phosphine oxides, so additional radical initiator types were evaluated. Experiments were conducted for two different α -amino ketones I-907 and I-184, and a thermal azo initiator AIBN. The choice for the alternative initiators was based on matching the wavelength of light used during inkjet printing and commercial availability. For the

alternative ink compositions, 1 wt% of the initiator was used, and the inks with 1 wt% Red305 were photopolymerized using the AKP inside a $20 \mu\text{m}$ glass cell. The absence of oxygen inside this glass cell allowed for the ink to be polymerized even with only 1 wt% of initiator (exact compositions given in Table S2). The cleavage of I-907 and I-307 form very similar radicals (SI Fig. S11), so both PIs are expected to influence the photopolymerization of the ink in the same way.

Fig. 5 shows both I-907 and I-307 induce strong reduction of the Red305 molecules during photopolymerization. In particular, the formation of the radical anion species is significant. The 10% permanent loss of the Red305 absorbance after ‘recovery’ is the same for both samples, approximately the same as the loss for the ink containing 1 wt% TPO and I-819. Despite similar losses in absorbance peaks, an additional decrease of almost 20% in FQY_{eff} is seen for the I-907 and I-307 samples. This increased loss in FQY_{eff} could be an indication of greater complex formation between the PI and the Red305 molecule, resulting in additional quenching of the FQY_{eff} .

Lastly, a thermal initiator was proposed. Thermal initiators are, next to PIs, a common way to induce free radical polymerization [36]. AIBN was chosen according to its availability and ease in use. The sample containing the 1 wt% AIBN ink was cured for 20 min at a temperature of 90°C . The chemical structure and decomposition reaction of AIBN is given in Fig. S12.

As can be seen in Fig. S13a, no reduced species are present after completion of the polymerization, and there was little effect, if any, on the absorbance of the Red305. It is expected the absence of persisting reduction of the Red305 molecules is due to the formation of fewer, less reactive radicals upon cleavage of the AIBN molecule. Considering the half-life time of AIBN of one hour at 85°C [37] compared to 36 sec for Irg 819 [38], during polymerization with AIBN at 90°C one can assume that significantly less radicals are formed at once, compared to the

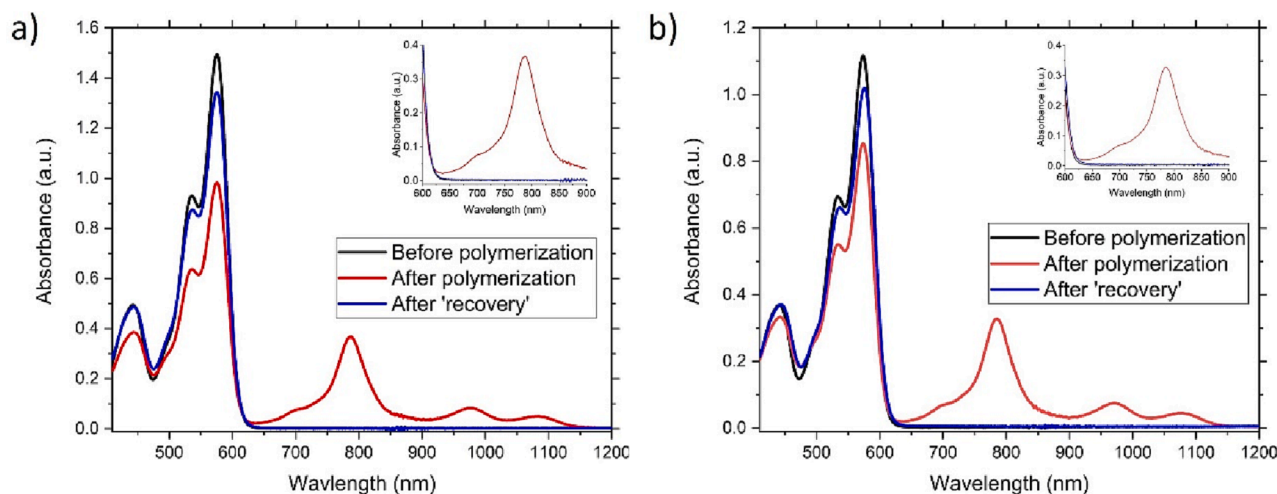


Fig. 5. Absorption spectra before and immediately after polymerization with the AKP inside a glass cell and after 'recovery' of the ink in ambient conditions. For the a) I-907 and b) I-307 inks.

immediate radical storm forming during UV exposure of the generated PIs. This difference in radical concentration during polymerization could be part of the reason for the difference in number of reduced species in the newly-polymerized samples. In addition, previous experiments show reversion of the reduced species upon heating, so any formation of reduced species during AIBN heating have all been repaired by the end of the polymerization process.

To evaluate the influence of light during polymerization of the AIBN ink, a glass cell filled with AIBN ink was heated for 20 min at 90 °C while simultaneously illuminating with an EXFO lamp. The resulting absorption spectra before and after polymerization and after 'recovery' are given in Fig. S13b. No indication of reduction of the Red305 molecules is seen.

Even though no obvious signals for reduced species are seen for the irradiated sample with AIBN, the final FQY_{eff} of this sample was affected; for the sample without irradiation the FQY_{eff} remained approximately 80%, where for the sample that was irradiated during photopolymerization a FQY_{eff} of only 65% was measured after polymerization. Since AIBN is both a thermal and PI (with an absorption maximum at 350 nm [39,40]), more radicals are expected to form upon irradiation with light. Additional radical formation could result in reduction of the Red305 molecules, which, upon heating could be recovered, resulting in the absence of the additional absorption peaks between 650 and 1200 nm but an effect on the FQY_{eff} . These results suggest an importance of the use of a lower intensity of light during photopolymerization, especially in inkjet printing devices not equipped with heating elements.

4. Conclusions

During photopolymerization of the fluorescent *Ink1*, nonfluorescent radical anion and fluorescent dianion species are formed on the Red305 molecules, being detrimental for the performance of luminescent solar concentrators. This reduction was found to occur for various commercially used light sources for photopolymerization, having both broad and narrow emission bands. The PIs in the ink composition appear to be the electron donors for this electron transfer, leading to the reduction of Red305. The thiols, as well as the acrylates, in the ink were found to protect the dye from reduction. The radical anion and dianion species were found to have a strong influence on the FQY_{eff} and color of the polymerized ink immediately after polymerization.

It appeared that over time, in the presence of oxygen, the radical anion and dianion species reverted, and a partial 'recovery' of the absorbance of Red305 was seen. However, after this 'recovery', for the

polymerized *Ink1* a permanent loss in FQY_{eff} of approximately 35% was observed, accompanied by a permanent 25% loss in the optical absorbance of the Red305 molecules. This permanent loss of absorbance by the Red305 molecules is most likely a consequence of increased probability of permanent photodegradation of the Red305 molecules when reduced to the dianion form. It is conjectured products of the photodegradation include a possible complex between the depleted PI and the Red305 molecules. The exact formation of this degradation or quenching product could be the goal of future work.

The influence of the PI was further elucidated by comparing the influence of different types of initiators. From this evaluation it was found that, next to the phosphine oxides TPO and I-819, the α -aminoketones, I-907 and I-307, and the hydroxyacetophenone, I-184, all resulted in a significant reduction of the Red305 molecules and a similar permanent loss in the absorption of these molecules.

Polymerization with a lower light intensity, reducing the rate of PI radical formation, was expected to mitigate the dianion formation, and therefore the photodegradation of the Red305 molecules, and the negative influence on the FQY_{eff} . This hypothesis was supported by the negligible influence on the FQY_{eff} when polymerizing the sample with the thermal initiator AIBN, forming radicals slower than the previously used PIs. Additional irradiation during the polymerization, resulting in faster radical formation of the AIBN initiator, did negatively affect the FQY_{eff} emphasizing the possible importance of the speed of radical formation on the degradation mechanisms of the Red305 molecules.

This research shows when the fluorescent dye Red305 encounters an excess of radicals, degradation mechanisms can occur that lead to a loss in optical density and quenching of the FQY_{eff} . These findings are not only useful for developing inkjet printable inks, but also for applications where the combinations of such dyes and radicals are desired.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.solener.2023.05.041>.

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