Near-Infrared Photoinitiating Systems: Photothermal Effect vs. Triplet-Triplet Annihilation - based UpConversion Polymerization

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ABSTRACT: NIR light induced polymerization has attracted more and more attention in the photopolymerization field due to the possibility to use safer and more penetrating wavelengths, reducing the hazardousness. Here, a novel perspective for the Free Radical Polymerization (FRP) of acrylate-based monomers based on Triplet-Triplet Annihilation UpConversion (TTA-UC) is proposed, avoiding the introduction of heavy metals, usually required in the TTA processes. Thermal imaging experiments and Real Time Fourier Transform Infrared (RT-FTIR) spectroscopy have been respectively used to record the temperature during NIR irradiation and measure the reactive function conversion. The competition between the TTA-UC and the NIR photothermal activation was investigated to compare the relative efficiency of both NIR processes. In view of the results obtained by the different methods, the photothermal effect seems to get the upper hand over the photoactivation of the system.

Near-Infrared (NIR) induced processes is one of the major research subjects since decades. The development of NIR lasers and LEDs technologies has triggered the possibility to replace the commonly used UV-Visible light in photochemistry. Indeed, a large part of reaction exploited until now relies on this range of wavelengths, i.e. 300 – 500 nm, because of the great amount of energy brought to the system. Nonetheless, problems of user's safety (skin and eyes damages)¹ as well as the environmental concerns induced by the use of UV light can be overcome by the use of Near-Infrared light. Through various studies, the NIR range has been finally subclassed into three different categories, called windows: the first one, called the biological transparency window², covers the 650 to 950 nm range, then at 1100 to 1350 nm comes the second window and finally the third one from 1600 to 1870 nm². A fourth one centred at 2200 nm seems to emerge according to the optical attenuation measurements but this point is still under discussion as the sensitivity of the detectors still needs to be improved². All these windows offer, at different scales, a deeper light penetration in materials, especially in biological tissues in which minimal absorption is observed. These advantages make that Near-Infrared light is more and more widely studied, in many research fields such as coatings³, photopolymerization^{4–6}, optics⁷, photochemically assisted synthesis⁸ and in medical applications. Notably, NIR light is a powerful tool that can be advantageously used for bioprinting while applying a minimally invasive or non-invasive approach⁹. NIR light can also be used for tissue imaging (detection of abnormalities)^{2,10–12}, for photodynamic therapy¹³ or for controlled drug release¹⁴. In this study, the focus will be made on the first NIR window (with an irradiation centered at 785 nm) as a powerful tool for photopolymerization.

Triplet-Triplet Annihilation (TTA), rare-earth ion (lanthanide) Upconversion (UC) and Two-Photon Absorption (TPA) constitutes the three main Upconversion processes known at present¹⁵. TTA-UC is based on nonlinear anti-Stokes shift process. Indeed, the TTA bimolecular mechanism, known since the beginning of the 1960s¹⁶, is based on the emission of a photon at a higher energy than the energy of the incident photon. This process requires two different species: the sensitizer (also called the donor) which absorbs the incident light and the annihilator (or acceptor) which emits at a shorter wavelength. The generally accepted mechanism for the process, presented in Scheme 1, can be decomposed into the following steps: first of all, the sensitizer, in the ground state ($^1[\text{Sen}]$), is excited by a long-irradiation wavelength to the singlet excited state ($^1[\text{Sen}]^*$) and converted by Intersystem Crossing (ISC) into a triplet excited state ($^3[\text{Sen}]^*$). Then, through a Triplet Energy Transfer (TET), the annihilator ($^1[\text{An}]$) is pumped to its triplet excited state ($^3[\text{An}]^*$). Finally, two annihilator triplets populate the first singlet excited state, which is at a higher energy than the singlet excited state of the sensitizer. Finally, the $^1[\text{An}]^*$ returns to its ground state through a radiative transition process. Remarkably, the generated light can be used to activate in depth an appropriate photoinitiator.

Scheme 1: General energetic diagram of the Triplet-Triplet Annihilation Upconversion (TTA-UC) mechanism between the sensitizer (Sen) and the annihilator (An)¹⁷

TTA-UC has been extensively regarded for its possibility to generate a blue light (short wavelength) upon irradiation with a less energetic light (e.g. at long wavelength such as the NIR light). Another great advantage of this chemistry is the generation of an in-deep light, increasing the size of the irradiated area, from the surface to the whole reaction vial. TTA-UC can be found in a wide range of applications including solar energy conversion^{18,19}, optical and electrical devices, polymeric materials²⁰.

Concerning the chemical compounds involved in TTA-UC when applied to photopolymerization, the sensitizer needs to have a sufficient solubility in the solvent/monomer used, should be carefully selected to greatly absorb around the emission wavelength of the irradiation source and should exhibit a small energy gap between the singlet and the triplet excited state, as well as an efficient Intersystem Crossing (ISC)¹⁵. To the best of our knowledge, a large majority of the sensitizers reported in the literature contains heavy metals such as palladium (Pd), platinum (Pt) but also zinc (Zn) among others^{1,4,21-9}. This might be considered as a brake on development in polymer chemistry, as this type of chemistry doesn't have a lot of industrial prospects and is still underrepresented in

applications. But a new trend consisting in developing a metal-free system is a key factor for a potential transfer to the polymer industry. A few studies devoted to this topic have already been reported in the literature (as exemplified with 2,4,5,7-tetraiodo-6-hydroxy-3-fluorone (TIHF) or BODIPY-derivatives structure)^{22–24}. As the main advantages, these organic compounds are more cost-efficient and environmentally benign compared to the “traditional” metalated sensitisers. Furthermore, organic compounds can easily be chemically modified so that their absorption bands can be finely tuned to perfectly fit with the emission wavelength of the irradiation sources.

As previously mentioned for the sensitiser, the annihilator needs to meet some requirements: the triplet excited state should be energetically-higher to that of the sensitiser’s one to maximise the anti-Stokes shift. The efficiency of the initiation step of the polymerization relies on its fluorescence quantum yield which have to be high and to recover the absorption band of the photoinitiator. Choice of polycyclic aromatic hydrocarbon compounds (PAHs) as annihilator is commonly done in the literature, and anthracenes or tetracenes can be cited as the most common structures^{15,17,19,25}.

As mentioned before, Near-Infrared (NIR) light has attracted much attention as it offers a deeper light penetration into the materials and constitutes a safer alternative to the UV light. Moreover, the lack of energy of the NIR light which is frequently mentioned as an obstacle for its utilisation in photopolymerization can be directly overcome by the TTA-UC principle itself. In this work, a combination of sensitiser and annihilator which can be used as an efficient NIR-to-blue Upconversion system and which does not contain heavy metals is proposed. Structures of the chemicals employed in these experiments are presented in the Chart 1 and in the Chart 2. Two Photoinitiating Systems (PISs) have been tested: a generally used Type I photoinitiator, Irgacure 784 (**I784**), and a Type II photoinitiator, camphorquinone (**CQ**) – ethyl 4-dimethylaminobenzoate (**EDB**). Concerning the annihilators, three molecules have been chosen based on the literature: 2,5,8,11-tetra-*tert*-butylperylene (**TTBP**)^{17,26}, 1-Chloro-9,10-*bis*(phenylethynyl)anthracene (**1-CBPEA**)^{15,27} and perylene^{15,28}. The results presented here are focused on three different sensitisers: 1-butyl-2-(2-[3-[2-(1-butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)]-diphenylamino-cyclopent-1-enyl]-vinyl)-3,3-dimethyl-3*H*-indolium tetrafluoroborate (**S2025**), 2-[2-[3-[2-(1,3-dihydro-1,3,3-trimethyl-2*H*-indol-2-ylidene)-ethylidene]-2-(1-phenyl-1*H*-tetrazol-5-ylsulfanyl)-1-cyclohexen-1-yl]-ethenyl]-1,3,3-trimethyl-3*H*-indolium chloride (**S0507**) and a Bodipy derivative. This latter has been synthesised following the pathway described in Supporting Information.

Chart 1: Monomer and photoinitiating systems used in this study

Chart 2: Sensitisers and annihilators investigated in this work

The first tests realised during this study consisted in irradiating different photoinitiating systems composed of a combination of sensitizers and annihilators, as well as one of the two PISs in the trimethylolpropane triacrylate (TMPTA) selected as the benchmark monomer. Monitoring of the polymerization kinetics was performed by Fourier Transform InfraRed spectroscopy (FTIR) combined with a thermal imaging camera. Polymerization experiments were carried out upon irradiation of the samples with a laser diode at 785 nm ($I_0 = 2.5 \text{ W/cm}^2$). To get a deeper insight into the system's characteristics, absorption and emission spectra of the systems were also measured. The different absorption spectra obtained for the different systems are presented in Supporting Information (See Figures S1 to S4), even though there are quite saturated due to the dimension of the cuvettes used for the analyses. The purpose of presenting them is to underline the two different absorption bands, the first one below 500 nm caused by the photoinitiating system and the second one above 680 nm due to the presence of the sensitizer. Emission spectra of the different systems made with S2025 as the sensitizer for an excitation at 785 nm are presented in Figure 1. No emission is detected for the Figure 1 (curve 5) as no annihilator has been introduced in the reactional system. This can be considered as a first proof that the annihilator is necessary to generate light through TTA-UC. Emission spectra of the systems with S0507 and Bodipy are presented in Supporting Information, Figures S3 and S4.

A picture of a sample taken during an experiment upon excitation @785 nm is also shown in the Figure 2.A. A scheme detailing what is observed in the Figure 2.A is presented in the Figure 2.B. Notably, presence of a blue emission upon irradiation at 785 nm is clearly detected in the Figure 2.A.

Figure 1: Visible emission spectra (in PMMA optic cuvette of 10×10 mm) of 0.5×10^{-3} %mol. S2025 in TMPTA with (1) 0.2 %mol. TTBP, 0.28 %mol. I784; (2) 0.2 %mol. Perylene, 0.28 %mol. I784; (3) 0.2 %mol. 1-CBPEA, 0.28 %mol. I784; (4) 0.2 %mol. TTBP, 1.8 %mol. CQ, 1.5 %mol. EDB; (5) 0.28 %mol. I784

Figure 2: (A) Picture of a sample made of 0.5×10^{-3} %mol. S2025, 0.2 %mol. TTBP, 0.28 %mol. I784 in TMPTA, taken under a 785 nm irradiation (irradiated by the top of the sample); (B) Simplified scheme of the sample environment when the picture was taken

At this point, several preliminary conclusions can be established in addition to the very promising initial results, i.e. the observation of a blue light generated by TTA-UC. The wavelengths of emission's peaks are in agreement with the literature, i.e. around 500 nm for the TTBP¹⁷, 445 nm for the perylene²⁴ and around 500 nm for the 1-CBPEA²². First of all, most of the photoinitiating systems examined in this work are appropriated for photoinitiation due to the good agreement between their respective absorptions and that of the emitted light originating from TTA-UC and generated by the different sensitizer/annihilator couples examined in this work (See Figures S1 to S4). Conversely, the CQ/EDB system has a narrow and slightly blue-shifted absorption band compared to that of the other systems comprising I784 (See curves 1 and 4 in Figure S3 or S4). The only exception is observed for the 1-CBPEA, for which a red-shifted emission is detected compared to that of the other annihilators and which make the emitted light of this annihilator less appropriate for photoinitiation with regards to the absorption of the different photoinitiating systems (Figure

1, curve 3). As a reminder, the camphorquinone absorbs between 425 and 495 nm with a maximum at 470 nm²⁹ whereas the I784 absorbs between 360 and 500 nm with two maximums at 380 and 470 nm. If the different annihilators only slightly differ by the absorption spectra, on the opposite, major differences can be found concerning their emission spectra. To illustrate this, TTBP seems to be a more appropriate annihilator than perylene as the generated light is brighter. A possible explanation to this phenomenon is the difference in the energy level of the two excited states caused by the *tert*-butyl substituent groups. The last observation is that, for S2025 and Bodipy derivative before normalisation, a higher emission peak is measured when the two-component system CQ/EDB is used, which can be explained by the fact that there is no absorption of the emitted light by the PIS (i.e. CQ is characterised by a lower absorption coefficient than I784).

In a second step, irradiation of the different photoinitiating systems with a laser diode at 785 nm was performed. Each irradiation has been recorded by the thermal imaging camera. The maximum temperature reached by the systems and the physical description of the polymer after irradiation are summarised in the Table 1. The formulations were in laminate in order to prevent the oxygen inhibition and preserve as far as possible the excited state of the TTA-UC system. By combining the temperatures reached with the absorption/emission spectra, the FTIR data and visual observations, TTBP or perylene and I784 could be selected as the most efficient annihilator and photoinitiator respectively. Indeed, none of the three formulations containing CQ/EDB has shown any double bond conversion and as suggested before, the anthracene derivative does not fully match with the PIS tested.

Table 1: Maximum temperatures reached by the different systems in TMPTA during irradiation with a laser diode at 785 nm, 2.5W/cm² and recorded by Thermal Imaging Camera and their polymerization state after irradiation (“+” indicates the polymerization of the entire formulation, “±” partly polymerized and “-“ its absence of polymerization).

Entry	System			T _{max} (°C)	Polymerization state after irradiation
1	S2025	TTBP	CQ/EDB	152	-
2			/	158	-
3			I784	>200	+
4		Perylene		166	±
5		1-CBPEA		155	±
6		/	/	148	-
7	S0507	TTBP	CQ/EDB	122	±
8			/	137	-
9			I784	153	+
10		Perylene		149	+
11		1-CBPEA		108	-
12		/	/	142	-
13	Bodipy	TTBP	CQ/EDB	70	-

14			/	N.D.	-
15			1784	77	-
16		Perylene		72	-
17		1-CBPEA		66	-
18		/	/	82	-
19	/	TTBP	1784	21	-
20		Perylene		24	-
21		1-CBPEA		27	-

N.D.: not determined.

Then, regarding the sensitizer, similar results, i.e. temperatures and physical states of the samples after irradiation, are obtained for S2025 and S0507 in terms of polymerization and temperatures reached by the samples (see Table 1, entries 1 to 12). Conversely, the Bodipy derivative proved to be inefficient irrespective of the annihilator and the PIS introduced (see Table 1, entries 13 to 18). Concerning the system in its integrality, the entries 3,4,5 compared to the entry 2 of the Table 1 prove that the three components, i.e. the sensitizer, the annihilator and the PI, are necessary to initiate the polymerization. This observation can also be based on the entries 9 and 10 compared to the entry 8 of Table 1. These results are confirmed by comparing the FTIR spectra before/after irradiation (See Figure 3.A and 3.B) and an example of thermal imaging recorded during an irradiation (Figure 3.C.) is presented in the Figure 3 using S0507. The totality of these results can be found in the Figure S4 to S6.

Figure 3: (A), (B): FTIR Spectra measured before (1) and after (2) 5 min of irradiation with a laser diode at 785 nm, 2.5 W/cm², RT, laminate. (A) 0.5.10⁻³ %_{mol}. S2025, 0.2 %_{mol}. TTBP, 0.28 %_{mol}. I784 in TMPTA ; (B) 0.5×10⁻³ %_{mol}. Bodipy, 0.2 %_{mol}. TTBP , 1.8 %_{mol}. CQ, 1.5 %_{mol}. EDB. (C) Example of experiment during thermal imaging irradiation of 3 %_{mol}. S0507, 0.2 %_{mol}. in TMPTA) placed in a 5

Considering the systematically reached samples (see Table 1, Figure 3.C.), a second without annihilator or formulated to confirm observed and generated by Triplet-Triplet Annihilation Upconversion was responsible of the polymerization. Actually, if the temperature doesn't exceed 100°C, no change in the viscosity or the physical state of the formulations could be observed, suggesting that a photothermal effect also plays a major role. As none of the formulation containing the Bodipy derivative as the sensitizer could show promising results, the rest of the study was focused on S2025 and S0507. Table 2 summarises the maximum temperatures reached during a 5 min irradiation at 785 nm and the physical state of the sample after irradiation.

Table 2: Maximum temperatures reached by the different systems in TMPTA during irradiation with a laser diode at 785 nm, 2.5W/cm² and recorded by Thermal Imaging Camera and their state after irradiation (“+” indicates the polymerization of the entire formulation, “±” of only a part and “-” its absence)

Entry	System			T _{max} (°C)	State after irradiation
1	S2025	TTBP	I784	>200	+
2			/	158	-
3		/	I784	>200	+
4	S0507	TTBP	I784	153	±
5				150	-
6		/	I784	174	±

Emission spectra of the systems have also been measured and the results are presented in Supporting Information (Figure S7). They corroborate the visual observations: a blue-light

could be clearly emitted when both the sensitiser (S2025 or S0507) and the annihilator (TTBP) were present in the formulation. The intensity difference of the emitted light, for the systems with and without I784, when S2025 was used as the sensitiser, is qualitatively quite huge and can be explained by the direct absorption of a part of the emitted light by the photoinitiator.

The polymerization, or its beginning, under Near-Infrared irradiation of the systems without TTBP (See Table 2, entries 3 and 6) confirmed that the sensitiser has also a heater effect, corroborated by the temperatures reached by the sensitisers alone (See Table 1, entries 6,12 and 18). To guarantee this fact and in order to have a better idea of the critical temperature, samples were placed in the oven during a few minutes at 100, 150 and 180°C. Simple visual observations (See Figure 4.A) and pictures of the samples before and after heating in the oven (Figure 4.B and C) are shown in Figure 4.

A

System	5 min at 100°C	7 min at 150°C	5 min at 180°C
Bodipy - TTBP - I784 in TMPTA	-	-	+
S2025 - TTBP - I784 in TMPTA	-	-	+
S0507 - TTBP - I784 in TMPTA	-	+	+

Figure 4: (A) Visual observations of the physical state of the different systems in TMPTA after few minutes in oven (+ indicates the polymerization of the entire formulation and - its absence). (B), (C): Pictures of formulation containing (1) $5 \cdot 10^{-3}$ %mol. Bodipy 3, 0.2 %mol. TTBP, 0.28 %mol. I784, (2) $5 \cdot 10^{-3}$ %mol. S2025, 0.2 %mol. TTBP, 0.28 %mol. I784 and (3) $5 \cdot 10^{-3}$ %mol. S0507, 0.2 %mol. TTBP, 0.28 %mol. I784 in TMPTA (B) before and (C) after five minutes at 180°C

At this point, it seems that the Triplet-Triplet Annihilation Upconversion occurs under Near-Infrared irradiation (see Figure 3.A., Figure S5.B. and S6), but this phenomenon strongly competes with the thermal effect of the sensitizer (see Figure 4.C. and Table 2, entries 3,6).

To be even more precise about the photothermal initiation, Differential Scanning Calorimetry (DSC) experiments have been carried out in order to simulate the thermal polymerization without light; the results are presented in the Figure 5. TMPTA has also been tested alone: its decomposition begins after 180°C (See Figure S9) and could influence the polymerization realised in the test Figure 4. Nevertheless, the decomposition's temperatures of the system with and without sensitizers reveal to be weaker than the TMPTA's one, suggesting the role of the photothermal effect. The theoretical enthalpy value for a complete conversion of the acrylate's double bonds ($\Delta H_{\text{theor}} = 78.2 \text{ kJ/mol}$)³⁰ has been used to calculate the conversions in reactive functions obtained by thermal process. Therefore, for the system without sensitizer, 54% of the reactive functions of the monomer has been converted, whereas 49 and 46% of conversions could be determined with S0507 and S2025, respectively. Considering that, due to its trifunctional character, reaching 100% of acrylate function conversion is impossible, these conversions are relatively high, confirming the photothermal effect.

Figure 5: Thermal polymerization experiments (heat flow vs heating temperature) between 25°C and 250 °C, heating rate: 10°C/min, under N₂, in TMPTA. (1) 0.28 %_{mol}. I784; (2) 0.5×10⁻³ %_{mol}. S2025, 0.2 %_{mol}. TTBP, 0.28 %_{mol}. I784.; (3) 0.5×10⁻³ %_{mol}. S0507, 0.2 %_{mol}. TTBP, 0.28 %_{mol}. I784.

The second information noticed in the DSC tests was the temperatures at which the polymerization began. As lower temperatures than those reached during irradiation (see Table 1 or 2) have been determined (see Figure 5), an incertitude about the major phenomenon involved in the polymerization process persists and the thermal effect can't be ruled out.

Conclusion:

This study presents promising results in the field of heavy metal-free Triplet-Triplet Annihilation UpConversion systems as a source of blue light while exciting the systems with a Near-Infrared irradiation. Polymerization has even been performed in some cases, with S2025 or S0507 as the sensitizers. Nevertheless, the temperatures reached during irradiation and the results obtained by DSC suggest that the photothermal effect prevail the TTA-UC effect, more specifically for the S2025.

Experimental part:

All commercial chemicals were selected with the highest purity available and used as received. 1-Butyl-2-(2-[3-[2-(1-butyl-3,3-dimethyl-1,3-dihydro-indol-2-ylidene)]-diphenylamino-cyclopent-1-enyl]-vinyl)-3,3-dimethyl-3*H*-indolium tetrafluoroborate (**S2025**) and 2-[2-[3-[2-(1,3-dihydro-1,3,3-trimethyl-2*H*-indol-2-ylidene)-ethylidene]-2-(1-phenyl-1*H*-tetrazol-5-ylsulfanyl)-1-cyclohexen-1-yl]-ethenyl]-1,3,3-trimethyl-3*H*-indolium chloride (**S0507**), purchased from Few Chemicals, and the Bodipy derivative, whose the synthesis pathway is available in Supporting Information, were used as Upconversion sensitizers. Concerning the annihilators, 2,5,8,11-tetra-*tert*-butylperylene (**TTBP**), was received from

Sigma Aldrich, as trimethylolpropane triacrylate (**TMPTA**). The two other annihilators, 1-Chloro-9,10-*bis*(phenylethynyl)anthracene (**1-CBPEA**) and perylene, were acquired from TCI chemicals, with the camphorquinone (**CQ**). Ethyl 4-dimethylaminobenzoate (**EDB**) and Irgacure 784 (**I784**) were purchased respectively from Lambson Ltd and BASF.

The percentage of Upconversion sensitizers and annihilators were calculated from the monomer content (in molar). The percentages of the different Photoinitiators/ Photoinitiator systems were calculated in weight from the monomer content but expressed in this paper in molar percentage for constancy.

For the polymerization experiments, a Thorlabs laser diode was used to irradiate the sample placed in a 5mL mold at 785 nm, 2.5 W.cm⁻² during 5 min, at room temperature (RT) and in laminate which just means with a piece of polypropylene at the top of the formulation. The temperature reached by the samples has been recorded during the irradiation time thanks to an infrared thermal imaging camera Fluke TiX500. Infrared absorption spectra have been acquired before and after irradiation using a Jasco 6600 Fourier Transform Infrared spectrometer (FTIR). The acrylate bands of interest (6100 – 6250 cm⁻¹) were compared before and after irradiation to confirm the polymerization. A Jasco V730 spectrophotometer has been used to measure the absorption of the formulation (in PMMA optic cuvette of 10 x 10 mm) in the visible – NIR region (between approximatively 400 and 1100 nm) with a scan speed of 400 nm/min. The emission spectra have been measured by a spectrofluorimeter Jasco FP-6200 under irradiation at 785 nm. A Mettler-Toledo DSC 1 differential scanning calorimeter has been employed to thermally polymerize the formulations placed in an aluminium 100 µL crucible, from 25 to 500°C with a heating rate of 10°C/min under nitrogen flow (100 mL/min).

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