Supporting Information

NIR-Sensitized Activated Photoreaction between Cyanines and Oxime Esters: Free-Radical Photopolymerization

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Materials

NIR sensitizers were received from FEW Chemicals GmbH (Bitterfeld-Wolfen, Germany) and Spectrum Info Ltd (Kiev, Ukraine). They were used without further purification. The monomers poly(ethylene glycol) methacrylate (PEGMA), tripropylene glycol diacrylate (TPGDA) and lauryl methacrylate (LMA) were purchased from SigmaAldrich. The inhibitor was removed by running through basic Al₂O₃ (Carl Roth GmbH) before it was transferred to the experiments. All other chemicals and solvents mentioned were received from SigmaAldrich with the required purity. No further purification occurred.

The oxime esters OXE-01 and OXE-02 were received from BASF as samples and used without further purification. COXE-15 is available from Hubei Gurun Technology Co., Ltd as GR-COXE-15. BTCF-OXE is available from FEW Chemicals GmbH as S 2674. Oxidation of \(3b\alpha Z_4X_1\) and \(3b\alpha Z_1X_4\) resulted in the respective products \(3b\alpha Z_4X_1-\text{ox}\) (\(\lambda_{\text{max}}\) in MeOH: 683 nm, \(\varepsilon_{\text{max}}\): 3.38×10⁵ M⁻¹ cm⁻¹) and \(3b\alpha Z_1X_4-\text{ox}\) available as S 2123 and S 2178 from FEW Chemicals GmbH, respectively. \(2bX_6\) was synthesized by anion exchange applying the procedure described previously. Thus, \(2bX_1\) and Li⁺[(CF₃SO₂)₂N] served as starting material, which were purchased with the highest available purity from FEW Chemicals GmbH and Iolitec GmbH, respectively. Mass spectrum of \(2bX_1\) taken in negative mode indicated successful ion exchange.

Table SI1: Summary of NIR sensitizers used, commercial trade name, and commercial source.

| Sens  | Trade name | Source                                      |
|-------|------------|---------------------------------------------|
| TR    | S 0991     | FEW Chemicals GmbH                         |
| 1bX₁  | S08731     | Spectrum Info                              |
| 2bX₁  | S 0772     | FEW Chemicals GmbH                         |
| 3bαZ₄X₁ | S 2025     | FEW Chemicals GmbH                         |
| 3bαZ₁X₄ | S 2026     | FEW Chemicals GmbH                         |
| 4ααZ₂  | S 2459     | FEW Chemicals GmbH                         |
| 4ββZ₃X₇ | S 2383     | FEW Chemicals GmbH                         |
| 5dZ₅X₅ | S10761     | Spectrum Info                              |
| 6cZ₃X₄ | S 2468     | FEW Chemicals GmbH                         |
| 6aZ₂   | S 2265     | FEW Chemicals GmbH                         |
| OXE-01 | OXE 01     | BASF                                        |
| OXE-02 | OXE 02     | BASF                                        |
| COXE-15 | GR-COXE-15 | Hubei Gurun Technology Co., Ltd             |
| BTCF-OXE | S 2674     | FEW Chemicals GmbH                         |
|        | S 2123     | FEW Chemicals GmbH                         |
|        | S 2178     | FEW Chemicals GmbH                         |
Instrumentation

New high-power NIR prototype emitting at 805 nm, 860 nm and 870 nm were used for the investigations. The NIR-LED prototype emitted at 805 nm with an exposure density of 1.2 W/cm² in a distance of 3 cm. It was gratefully received from Phoseon Ltd. It exhibited a size 8 cm x 13 cm x 3 cm. The available exposure area covers 1.4 cm² in the aforementioned distance.

A NIR-LED prototype emitting at 860 nm with an exposure density of 1.5 W/cm² in a distance of 2 cm was gratefully received from EASYTEC GmbH. It exhibits a size 10 cm x 20 cm x 5 cm. The available exposure area covers 3 cm² in the aforementioned distance.

A NIR-LED prototype emitting at 870 nm with an exposure density of 1.2 W/cm² in a distance of 1 cm was gratefully received from EASYTEC GmbH and used for real-time FTIR experiments due to the smaller size. Figure SI1 shows a general picture of all three NIR-LEDs. The available exposure area covers 1 cm² in the aforementioned distance.

![Figure SI1: Emission spectra of 805nm NIR-LED (red), Emission spectra of 860nm NIR-LED (black), and (c) Emission spectra of 870nm high-power NIR-LED (blue). Emission spectra and intensity were taken by a fiber optical spectrometer from Ocean Optics (USB4000).](image-url)
Spectra of the dissolved sensitizers in methanol were measured with a Cary 5000 from Agilent in 1x1 cm quartz cuvettes (Figure SI2).

Figure SI2: (a) VIS-NIR spectra of sensitizers with six-membered ring in the middle position, (b) UV-VIS-NIR spectra of sensitizers with five-membered ring in the middle position, (c) UV-VIS-NIR spectrum of sensitizer without ring in the middle position.
Real time FTIR

A regular real-time FTIR setup\textsuperscript{[2]} was used to measure radical photopolymerization of TPGDA with different sensitizers and the oxime ester. The samples were prepared by dissolving the NIR sensitizer (0.05 wt\%) and oxime ester in the TPGDA. Exposure occurred with the 805nm NIR-LED as aforementioned disclosed in distance of 3.0 cm and 870nm NIR-LED aforementioned disclosed in distance of 1.0 cm. Spectra were taken in ATR mode. The films had a thickness of 10 µm. The peak area at 810 cm\(^{-1}\) was used to determine the conversion of double bounds and the carbonyl group band of the acrylates (1720 cm\(^{-1}\)) were used as reference (Figure SI3).

Figure SI3: (a) Radical photopolymerization of TPGDA with different sensitizers (0.05 wt\%) while concentration of OXE-01 was not changed (2 wt\%), (b) radical photopolymerization of TPGDA with 6aZz (0.05 wt\%) and different oxime esters (2 wt\%), (c) radical photopolymerization of TPGDA with 6aZz (0.05 wt\%) and OXE-01 applying different concentrations of OXE-01, (d) radical photopolymerization of TPGDA with different sensitizers (0.05 wt\%) and OXE-01 (2 wt\%) using different intensity NIR LED. NIR LED sources emitted at 805nm (intensity: of 1.2 W·cm\(^{-2}\)) and 790nm (intensity: 30 mW·cm\(^{-2}\)). Data were taken with a Bruker Vertex 70 in ATR-mode in real time.
**Photo-DSC**

**UV exposure of oxime ester with 395nm LED**

A regular photo-DSC setup\(^5\) was used to determine the photoinitiation efficiency of the oxime ester photoinitiator systems in the monomers giving the opportunity to run the experiment at the same temperatures, that is 40°C. This setup also helped to operate at isothermal conditions. Thus, each sample comprising TPGDA and the respective oxime ester went through a syringe filter before used in the experiment. The UV-LED emitting at 395nm was used for all exposure experiments (output 0.1 W/cm\(^2\)). The light generated was collected with a lens and projected into a y-fiber, which was connected with the head of the DSC (Q2000 from TA-Instruments). The output of UV light of each fiber arm was adjusted. The LED-source was synchronized with the DSC by a shutter system placed between the fiber and the lens. Details about the shutter system are given in ref.\(^5\). The photo-DSC measurements in Fig. SI4 using OXE-01, OXE-02, COXE-15 and BTCF-OXE as the initiator at the concentration of 0.05 wt% in TPGDA were carried out at the same isothermal conditions (40°C). The conversion of TPGDA was calculated by the theoretical heat enthalpy for the polymerization of acrylates given in the literature\(^6\)–\(^8\), i.e. 83.6 kJ/mol for each acrylate bond.

![Figure SI4: Photo-DSC measurements of TPGDA polymerization with different oxime esters (0.05 wt%) applying an UV LED source emitting at 395 nm (intensity: 0.1 W·cm\(^{-2}\)). Data were taken with a DSC Q2000 from TA-Instruments.](image)

**NIR Exposure of NIR sensitizer and Oxime ester with NIR LED**

A regular photo-DSC setup\(^5\) was used to determine the photoinitiation efficiency of the NIR photoinitiator systems in the monomers giving the opportunity to run the experiment at different temperatures to approve the necessity of additional heat needed to activate the process; that is 40°C, 60°C and 80°C. This setup also helped to operate at isothermal conditions. Thus, each sample comprising TPGDA, OXE-01 and the respective sensitizer went through a syringe filter before used in the experiment. The
aforementioned NIR-LED from Phoseon emitting at 805 nm was used for all exposure experiments (intensity: 0.2 W/cm²). The light generated was collected with a lens and projected into a y-fiber, which was connected with the head of the DSC (Q2000 from TA-Instruments). The output of NIR light of each fiber arm was adjusted. The LED-source was synchronized with the DSC by a shutter system placed between the fiber and the lens. Details about the shutter system are given in ref.[5]. The photo-DSC measurements in Figure SI5 using 6aZ₂, 3bαZ₄X₁, 4ααZ₂ and 6cZ₃X₃ as the sensitizer (0.05wt%) and OXE-01 as the initiator (2.0 wt%) in TPGDA were carried out at different isothermal conditions (40°C, 50°C, 80°C). The heat flow nearly didn’t change meaning that there was nearly no polymerization activity.

Figure SI5: Photo-DSC measurements of samples comprising TPGDA, 6aZ₂, 3bαZ₄X₁, 4ααZ₂ and 6cZ₃X₃ (0.05wt%) and OXE-01 (2.0 wt%) at different temperatures (40°C, 60°C, 80°C), intensity of the LED device: 0.2W·cm⁻².
**LC-MS**

Reaction products were analyzed with a QTOF-LCMS system (G6530B) from Agilent using Dual AJS ESI as the ion source. As a column Hypersil C4 (125 x 4mm) from Thermofischer Scientific was used with acetonitrile/water (80:20) as eluent. After 20 minutes the ratio was changed to 95:5. The photoproducts of 3baZ4X1, 3baZ6X4 were generated by exposure of the initiator system comprising 3baZ4X1 and 3baZ6X4 (0.05wt%) and OXE-01 (2.0 wt%) with the LED prototype (1.2 W·cm⁻², 5min) in PEGMA under continuous nitrogen gas flow. The polymerized PEGMA being soluble in MeOH was removed from the photoproducts of the initiator system using column chromatography with methanol as the eluent and silica (silica gel 60 from Carl Roth) as the column material. This sample was diluted with acetonitrile for further LC-MS measurement. Oxidized Photoproducts were also expected since the exposure was not completely free from air. This also includes sample preparation. The reference products 3baZ4X1-ox (S 2178) and 3baZ6X4-ox (S 2123) were dissolved in methanol and injected in this system to compare their retention time and molecular ions with the respective solutions exposed. Figure S6 shows the results.

Figure S6. LC-Signals of the photoproducts after exposure of either 3baZ4X1, or 3baZ6X4 as sensitizer while OXE-01 served as initiator. Exposure occured with the 805nm NIR LED device (1.2 W·cm⁻²; 10 minutes exposure time). The films obtained after exposure of PEGMA were extracted with acetone before transferred to the LS-MS measurement. The remaining polymer was finally removed by column chromatography. The oxidized reference materials 3baZ4X1-ox and 3baZ6X4-ox were used without further treatment for the LC-MS experiment.

**Cyclic voltammetry**

The oxidation potential of the sensitizers was recorded by cyclic voltammetry (VERSASTAT4-400 from AMETEK served as potentiostat) in acetonitrile (c_sens= 10⁻³ mol/L) with tetrabutylammonium hexafluorophosphate from Aldrich (0.1 mol/L) as a supporting electrolyte against ferrocene as an external standard. The data were taken with a scanning rate of 0.015 V·s⁻¹ using platinum disc as a working electrode and Ag/AgCl as reference electrode[^9].
**Photochemical conversion**

The conversion of **TPGDA** was analyzed by FTIR measurements using the band at 810 cm\(^{-1}\) for the decrease of acrylic double bonds and 1720 cm\(^{-1}\) of the carbonyl group as the reference. The sample contained the sensitizer **6aZ**\(_2\) (0.5 wt\%) and different oxime esters (2.0 wt\%) as coinitiators. The samples were prepared as films with a thickness 160 \(\mu\)m with two pieces of glass and were irradiated with the LED emitting at 805 nm / \(I = 1.2 \text{ W}\cdot\text{cm}^{-2}\) and 860 nm / \(I = 1.5 \text{ W}\cdot\text{cm}^{-2}\).

Table SI2: Conversion of **TPGDA** obtained after exposure the system comprising **6aZ**\(_2\) (0.5 wt\%) and different oxime esters (2 wt\%) using the 805nm LED device (1.2 W·cm\(^{-2}\)) and 860nm LED device (1.5 W·cm\(^{-2}\)). Exposure time was 5 min.

| Oxime ester | Conversion of **TPGDA** with 805nm LED | Conversion of **TPGDA** With 860nm LED |
|-------------|--------------------------------------|--------------------------------------|
| OXE-01      | 100%                                 | 100%                                 |
| OXE-02      | 100%                                 | 100%                                 |
| COXE-15     | 67%                                  | 85%                                  |

**Bleaching rate**

The samples comprised the monomer **PEGMA**, the sensitizer (0.05 wt\%) and the oxime ester OXE-01 (2 wt\%) and were irradiated with the LED device 805nm (1.2 W·cm\(^{-2}\) / 5 minutes) and 860nm (1.5 W·cm\(^{-2}\) / 5 minutes). under nitrogen atmosphere. After exposure the polymer of **PEGMA** was dissolved in methanol (10.0 to 20 mg in 2mL) to achieve a maximum absorbance of the sensitizer and its photoproducts around 0.3 to 1.0. The Vis-NIR spectra were carried out using the Cary 5000 from Agilent in 1 x 1 cm quartz cuvettes. The spectra of the bleached sensitizers (Figure SI7) are related to the absorbance of the sensitizer with the same concentration before NIR exposure.
Figure SI7: Vis-NIR-absorption of different sensitizers (0.05 wt%) in PEGMA comprising OXE-01 (2 wt%) before and after exposure with the 860nm NIR LED device (1.5 W·cm⁻²; 5 minutes). After completing of exposure, the sample was dissolved in methanol after LED exposure using a 1cm x 1cm cuvette.
Bleaching kinetics

Figure SI8 depicts bleaching kinetics of $3\text{b}a\text{Z}_3\text{X}_1$ and $3\text{b}a\text{Z}_1\text{X}_4$ (3.5×10^{-6} mol/L) with OXE-01 (2.0×10^{-5} mol/L) using LMA as monomer and solvent. High-power LED emitting 805nm with an exposure density of 1.2W·cm^{-2} was applied. The measurement was done using a 1cm x 1cm cuvette.

![Bleaching kinetics](image)

Figure SI8: Vis-NIR absorption spectra of LMA solution comprising (a) $3\text{b}a\text{Z}_3\text{X}_1$ (3.5×10^{-6} mol·L^{-1}), (b) $3\text{b}a\text{Z}_1\text{X}_4$ (3.5×10^{-6} mol·L^{-1}) and OXE-01 (2.0×10^{-5} mol·L^{-1}) before and after exposure with the NIR LED device at 805 nm (1.2 W·cm^{-2}) applying different exposure time. The measurement was done in a 1cm x 1cm cuvette.

Determination of the temperature for thermal initiation of polymerization $T_i$

The thermal initiation temperature $T_i$ was determined by DSC experiments (Q 300 from TA instruments). The samples were heated with a rate of 10 K/min up to 250°C to determine the onset-point of the exothermal peak where polymerization starts. The samples comprised the sensitizer $6\text{aZ}_2$ (0.05 wt%) and different oxime esters (2.0 wt%) in TPGDA. The samples also comprised the different sensitizers (0.05 wt%) and OXE-01 (2.0 wt%) in TPGDA of Table 1.

Table SI3: The initial temperature of thermal polymerization ($T_i$) of TPGDA comprising the NIR sensitizer $6\text{aZ}_2$ (0.5 wt%) and different oxime esters as (2 wt%)

| Oxime ester | $6\text{aZ}_2$ | $T_i$ of TPGDA |
|-------------|----------------|----------------|
| OXE-01      | -              | 65             |
|             | +              | 91             |
| OXE-02      | -              | 68             |
|             | +              | 102            |
| COXE-15     | -              | 78             |
|             | +              | 109            |
| BTCF-OXE    | -              | 173            |
|             | +              | 186            |


Temperature measurement

The temperature generated by sensitizers were measured. The samples comprising the monomer TPGDA, the sensitizer (0.5 wt%) and the oxime ester OXE-01 (2 wt%) were irradiated with the respective LED device from either Phoseon emitting at 805nm with an intensity of 1.2 W·cm⁻² or EASYTECH emitting at 860nm with an intensity of 1.5W·cm⁻² (Figure SI9). We also measured the temperature of the sample comprising 2wt% OXE-01 and 0.5 wt% 6aZ₂, respectively, to compare the heat generated by a high power NIR LED with the heat generated by sensitizer 6aZ₂ (Figure SI9a). The samples comprising the monomer TPGDA, the sensitizer 6aZ₂ at different concentration and the oxime ester COXE-15 (2 wt%) were irradiated with the LED device from Phoseon at 805nm (Figure SI9b). The thickness of the film was 160µm using spacers to maintain comparable thickness for all experiments while the sample was covered with an additional glass plate to keep nonplanarity artifacts on a low level. Irradiation time was 600s. A NIR sensitive camera (testo 0563 0885 V7) was used to record the temperature changes.

![Figure SI9](image)

Figure SI9: (a) Temperature increase (matrix: TPGDA) upon NIR exposure of a sample comprising OXE-01 (2 wt%) and no sensitizer (black line), and a sample comprising 6aZ₂ (0.5 wt%). (b) temperature of the samples comprising 6aZ₂ at different concentration while COXE-15 (2 wt%) was kept at the same concentration.

Table SI4: The temperature (T/°C) generated by sensitizers in the samples comprising the monomer TPGDA, the sensitizer (0.5 wt%) and OXE-01 (2 wt%).

| Sensitizers (0.5 wt%) | OXE-01(2 wt%) | T /°C 805nm LED | T /°C 860nm LED |
|----------------------|---------------|-----------------|-----------------|
| 6aZ₂                 | +             | 110             | 138             |
| 6aZ₂                 | -             | 116             | /               |
| -                    | +             | 40              | /               |
| 4aαZ₂                | +             | 97              | 109             |
| 6cZ₂X₃               | +             | 108             | 132             |
| 3bαZ₁X₁              | +             | /               | 125             |
| 3bαZ₁X₄              | +             | /               | /               |
Table S15: Temperature (T/°C) generated in the samples comprising the monomer **TPGDA, 6aZ2 (S 2265)** at different concentrations, and **COXE-15** (2 wt%)

| Concentration of 6aZ2 (S2265) | COXE/15(2 wt%) | T /°C 805nm LED |
|-------------------------------|----------------|-----------------|
| 0.05%                         | +              | 66              |
| 0.1%                          | +              | 82              |
| 0.2%                          | +              | 93              |
| 0.5%                          | +              | 98              |
| 1%                            | +              | 107             |

**Laser exposure**

a) **Fiber-coupled laser**: Fiber-coupled Laser exposure was carried out with a NIR laser emitting at 974 nm (Changchun New Industries Optoelectronics Technology Co., Ltd.; CNI-980-25 W-5-FC-A1-TTL1-MM400SMA, L1). The sample contained the sensitizer **TR** (0.05 wt%) and **OXE-01** (2.0 wt%) as coinitiator. The samples were prepared as films with a thickness 160µm with two paces of glass and were irradiated for 10 s (P<sub>output</sub> = 23 W, I = 125 W cm<sup>2</sup>). The conversion of **TPGDA** was analyzed by FTIR measurements using the band at 810cm<sup>-1</sup> for the decrease of acrylic double bonds and 1720cm<sup>-1</sup> of the carbonyl group as the reference. The results showed no conversion. A second laser with more power was used to verify this result (see b)).

b) **Line-shaped focused laser**: Laser exposure was pursued using a NIR laser emitting at 980 nm with line shaped focus (Laserline LDL 40-400, line width 1.5 mm, line length 31.5 mm). The samples were prepared as mentioned above and were irradiated with the laser emitting at 980nm (scan speed = 0.004 m s<sup>-1</sup>, P<sub>output</sub> = 300 W). The irradiation of the sample showed no conversion of **TPGDA**.
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