## **Supporting Information**

# One-Component Cationic Photoinitiators Based on Coumarin Scaffold Iodonium Salts as Highly Sensitive Photoacid Generators for 3D Printing IPN Photopolymers under Visible LEDs Source

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## 1. Structure and purity of obtained products confirmed by NMR and LC-MS analysis.

## Materials and methods

7-methoxy-4-methylcoumarin-3-yl-phenyliodonium hexafluorophosphate derivatives were obtained following recently published procedure<sup>1</sup>. All reagents for synthesis were supplied from commercial sources and used without any further purification.

Structure and purity of synthesised compounds was confirmed with nuclear magnetic resonance spectra, mass spectrometry and liquid chromatography. <sup>1</sup>H NMR spectra were recorded in DMSO-D<sub>6</sub> on Advance III HD 400 MHz (Bruker) spectrometer. Chemical shifts were reported in parts per million ( $\delta$ ) and referenced to residual protonated solvent peak ( $\delta$  = 2.50 ppm in <sup>1</sup>HNMR).

<sup>31</sup>P NMR spectra were recorded in DMSO-D6 on Advance III HD 400 MHz (Bruker) spectrometer. Chemical shifts were reported in parts per million ( $\delta$ ) and referenced to 85% phosphorous acid peak ( $\delta$  = 0 ppm in <sup>31</sup>P NMR).

LC-MS analyses were obtained on LCMS-2020 (Shimadzu) with ESI ionization method.

Elemental analyses were carried out using Vario El III CHNS Analyzer.

	<sup>1</sup> H NMR (400 MHz, DMSO) $\delta$ 8.17 (dd, <i>J</i> = 8.3, 1.0 Hz, 2H), 8.01 (d, <i>J</i> = 9.0 Hz, 1H), 7.68 (t, <i>J</i> = 7.4 Hz, 1H), 7.53 (dd, <i>J</i> = 10.8, 4.8 Hz, 2H), 7.13 (d, <i>J</i> = 2.5 Hz, 1H), 7.09 (dd, <i>J</i> = 9.0, 2.5 Hz, 1H), 3.91 (s, 3H), 2.99 (s, 3H).		
7M-P	MS (ESI) m/z(%): 393 ([M] <sup>+</sup> ,98.5%)		
	Anal. Calcd.: C 37,94%; H 2,62% Found: C 38,51% ;H 3,33%		
	<sup>1</sup> H NMR (400 MHz, DMSO) δ 8.37 – 8.32 (m, 2H), 8.06 – 7.94 (m, 3H), 7.14 (d, <i>J</i> = 2.5 Hz, 1H), 7.10 (dd, <i>J</i> = 9.0, 2.5 Hz, 1H), 3.91 (s, 3H), 2.98 (s, 3H).		
7M-CN-P	MS (ESI) m/z(%): 418 ([M]⁺, 95%)		
	Anal. Calcd.: C 38,39% H 2,33% N 2,49% Found: C 37,47% H 3,11% N 2,86%		
	<sup>1</sup> H NMR (400 MHz, DMSO) δ 8.44 – 8.38 (m, 2H), 8.31 – 8.25 (m, 2H), 8.03 (d, <i>J</i> = 9.0 Hz, 1H), 7.14 (d, <i>J</i> = 2.5 Hz, 1H), 7.11 (dd, <i>J</i> = 9.0, 2.5 Hz, 1H), 3.91 (s, 3H), 2.99 (s, 3H).		
7M-NO <sub>2</sub> -P	MS (ESI) m/z(%): 438 ([M]+ ,95.5%)		
	Anal. Calcd.: C 35,01% H 2,25% N 2,40% Found: C 34,07% H 3,26% N 2,32%		



## 2. <sup>1</sup>H NMR spectra of synthesized compounds.



Fig. S1: <sup>1</sup>H NMR of 7M-P.





Fig. S5: <sup>1</sup>H NMR of 7M-iPr-P.

<sup>31</sup>P NMR spectra of synthesized compounds.



Fig. S6: 31P NMR of 7M-P.



0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 Chemical shift (ppm)



Fig. S8: <sup>31</sup>P NMR of 7M-NO<sub>2</sub>-P.



0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 Chemical shift (ppm)





Fig. S10: <sup>31</sup>P NMR of 7M-iPr-P



## 3. Theoretical UV spectra calculated by the uB3LYP / LANL2DZ method



4. Steady state photolysis for the cationic photoinitiators under low power of UV-A LED with the maximum of emission at 365nm in acetonitrile.



**Fig. S11:** Photolysis of 7M-P in acetonitrile under 365nm (6.78 mW/cm<sup>2</sup>); concentration [7M-P] = 4.24 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].



Fig. S13: Photolysis of 7-M-NO<sub>2</sub>-P in acetonitrile under 365nm (6.78 mW/cm<sup>2</sup>); concentration [7-M-NO<sub>2</sub>-P] =  $3.81 \cdot 10^{-5}$  [mol/dm<sup>3</sup>].



**Fig. S15:** Photolysis of 7-M-iPr-P in acetonitrile under 365nm (6.78 mW/cm<sup>2</sup>); concentration [7-M-iPr-P] = 3.62 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].



**Fig. S12:** Photolysis of 7-M-CN-P in acetonitrile under 365nm (6.78 mW/cm<sup>2</sup>); concentration [7-M-CN-P] = 3.91 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].



Fig. S14: Photolysis of 7-M-Me-P in acetonitrile under 365nm (6.78 mW/cm<sup>2</sup>); concentration [7-M-Me-P] = 3.84 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].





**Fig. S16:** Photolysis of 7M-P in acetonitrile under 405nm (304.5 mW/cm<sup>2</sup>); concentration [7M-P] = 4.24 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].



Fig. S18: Photolysis of 7-M-NO<sub>2</sub>-P in acetonitrile under 405nm (304.5 mW/cm<sup>2</sup>); concentration [7-M-NO<sub>2</sub>-P] =  $3.81 \cdot 10^{-5}$  [mol/dm<sup>3</sup>].



Fig. S20: Photolysis of 7-M-iPr-P in acetonitrile under 405nm (304.5 mW/cm<sup>2</sup>); concentration [7-M-iPr-P] =  $3.62 \cdot 10^{-5}$  [mol/dm<sup>3</sup>].



Fig. S17: Photolysis of 7-M-CN-P in acetonitrile under 405nm (304.5 mW/cm<sup>2</sup>); concentration [7-M-CN-P] =  $3.91 \cdot 10^{-5}$  [mol/dm<sup>3</sup>].



Fig. S19: Photolysis of 7-M-Me-P in acetonitrile under 405nm (304.5 mW/cm<sup>2</sup>); concentration [7-M-Me-P] = 3.84 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].

6. Steady state photolysis for the cationic photoinitiators under low power of visible LED with the maximum of emission at 405nm in acetonitrile - comparison of the absorbance spectrum of compounds 7-M-CN-P and 7-M-NO<sub>2</sub>-P at current 87 and 304.5 mW/cm<sup>2</sup>



**Fig. S21:** Photolysis of 7-M-CN-P in acetonitrile under 405nm (87 mW/cm<sup>2</sup>); concentration [7-M-CN-P] = 3.91 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].



Fig. S23: Profiles illustrating changes in absorbance over time of 7-M-CN-P at 365nm, upon exposure to LED@405nm and different current 87 and 304.5 mW/cm<sup>2</sup>



Fig. S22: Photolysis of 7-M-NO<sub>2</sub>-P in acetonitrile under 405nm (87 mW/cm<sup>2</sup>); concentration [7-M-NO<sub>2</sub>-P] = 3.81 · 10<sup>-5</sup> [mol/dm<sup>3</sup>].



Fig. S24: Profiles illustrating changes in absorbance over time of 7-M-NO<sub>2</sub>-P at 365nm, upon exposure to LED@405nm and different current 87 and 304.5 mW/cm<sup>2</sup>

7. Cyclic voltammetry curves showing oxidation and reduction processes of the cationic photoinitiators derivatives in acetonitrile.



Fig. S25: Cyclic voltammogram curves of the 7M-P reduction in acetonitrile.



Fig. S27: Cyclic voltammogram curves of the 7-M-NO<sub>2</sub>-P reduction in acetonitrile.



reduction in acetonitrile.



Fig. S26: Cyclic voltammogram curves of the 7-M-CN-P reduction in acetonitrile.



Fig. S28: Cyclic voltammogram curves of the 7-M-Me-P reduction in acetonitrile.

- 8. Photoinitiating ability of the coumarin-based iodonium photoinitiators in the role of photoinitiators in cationic photopolymerization (CP)
- 8.1. Applicability of Sylanto derivatives for on-line monitoring progress of ring opening photopolymerization of epoxy CADE monomer (ROP-CP) under UV-LED 365 nm and current 27 mW/cm<sup>2</sup>



Fig. S30: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (27 mW/cm<sup>2</sup>) in composition with 7M-P compound as the photoinitator.



Fig. S32: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (27 mW/cm<sup>2</sup>) in composition with 7-M-NO<sub>2</sub>-P compound as the photoinitator.



Fig. S31: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (27 mW/cm<sup>2</sup>) in composition with 7-M-CN-P compound as the photoinitator.



**Fig. S33:** FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (27 mW/cm<sup>2</sup>) in composition with 7-M-Me-P compound as the photoinitator.





8.2. Applicability of Sylanto derivatives for on-line monitoring progress of ring opening photopolymerization of epoxy CADE monomer (ROP-CP) under UV-LED 365 nm and current 95 mW/cm<sup>2</sup>



Fig. S35: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (95 mW/cm<sup>2</sup>) in composition with 7M-P compound as the photoinitator.



Fig. S37: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (95 mW/cm<sup>2</sup>) in composition with 7-M-NO<sub>2</sub>-P compound as the photoinitator.





Fig. S36: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (95 mW/cm<sup>2</sup>) in composition with 7-M-CN-P compound as the photoinitator.



Fig. S38: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 365 nm irradiation (95 mW/cm<sup>2</sup>) in composition with 7-M-Me-P compound as the photoinitator.



8.3. Applicability of Sylanto derivatives for on-line monitoring progress of ring opening photopolymerization of epoxy CADE monomer (ROP-CP) under UV-LED 405 nm and current 435 mW/cm<sup>2</sup>



Fig. S40: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 405 nm irradiation (435 mW/cm<sup>2</sup>) in composition with 7M-P compound as the photoinitiator.



Fig. S42: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 405 nm irradiation (435 mW/cm<sup>2</sup>) in composition with 7-M-NO<sub>2</sub>-P compound as the photoinitiator.





Fig. S41: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 405 nm irradiation (435 mW/cm<sup>2</sup>) in composition with 7-M-CN-P compound as the photoinitiator.



**Fig. S43:** FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 405 nm irradiation (435 mW/cm<sup>2</sup>) in composition with 7-M-Me-P compound as the photoinitiator.

← Fig. S44: FT-IR spectra before and after photopolymerization of CADE monomer under UV-LED 405 nm irradiation (435 mW/cm<sup>2</sup>) in composition with 7-M-iPr-P compound as the photoinitiator.

8.4. Applicability of Sylanto derivatives for on-line monitoring progress of ring opening photopolymerization of vinyl ether TEGDVE monomer (VE-CP) under UV-LED 365 nm and current 13.5 mW/cm<sup>2</sup>



Fig. S45: FT-IR spectra before and after photopolymerization of TEGDVE under UV-LED 365 nm irradiation (13.5 mW/cm<sup>2</sup>) in composition with 7M-P.



Fig. S47: FT-IR spectra before and after photopolymerization of TEGDVE under UV-LED 365 nm irradiation (13.5 mW/cm<sup>2</sup>) in composition with 7-M-NO<sub>2</sub>-P.





Fig. S46: FT-IR spectra before and after photopolymerization of TEGDVE under UV-LED 365 nm irradiation (13.5 mW/cm<sup>2</sup>) in composition with 7-M-CN-P



Fig. S48: FT-IR spectra before and after photopolymerization of TEGDVE under UV-LED 365 nm irradiation (13.5 mW/cm<sup>2</sup>) in composition with 7-M-Me-P.

⇐ Fig. S49: FT-IR spectra before and after photopolymerization of TEGDVE under UV-LED 365 nm irradiation (13.5 mW/cm<sup>2</sup>) in composition with 7-M-iPr-P.

8.5. Applicability of Sylanto derivatives for on-line monitoring progress of ring opening photopolymerization of vinyl ether TEGDVE monomer (VE-CP) under UV-LED 405 nm and current 217.5 mW/cm<sup>2</sup>



Fig. S50: FT-IR spectra before and after photopolymerization of TEGDVE monomer under UV-LED 405 nm irradiation (217.5 mW/cm<sup>2</sup>) in composition with 7M-P compound as the photoinitiator.



**Fig. S52:** FT-IR spectra before and after photopolymerization of TEGDVE monomer under UV-LED 405 nm irradiation (217.5 mW/cm<sup>2</sup>) in composition with 7-M-NO<sub>2</sub>-P compound as the photoinitiator.





Fig. S51: FT-IR spectra before and after photopolymerization of TEGDVE monomer under UV-LED 405 nm irradiation (217.5 mW/cm<sup>2</sup>) in composition with 7-M-CN-P compound as the photoinitiator.



Fig. S53: FT-IR spectra before and after photopolymerization of TEGDVE monomer under UV-LED 405 nm irradiation (217.5 mW/cm<sup>2</sup>) in composition with 7-M-Me-P compound as the photoinitiator.

← Fig. S54: FT-IR spectra before and after photopolymerization of TEGDVE <sup>monomer</sup> under UV-LED 405 nm irradiation (217.5 mW/cm<sup>2</sup>) in composition with 7-M-iPr-P compound as the photoinitiator.

9. Photopolymerization of bis[1-Ethyl(3-oxetanyl)]methyl ether (OXT-221) and trimethylolpropane triglycidyl ether (TMPTGE) monomer by Isothermal differential scanning calorimetry (photo-DSC)



## 10. DSC for determination of thermal stability

## DSC for determination of thermal stability:

The thermal stability of the iodonium salts was tested at the DSC 204 Phoenix from Netzsch, Germany. 5 mg of the sample was heated up from  $0 \circ C$  to 250  $\circ C$  with a temperature ramp of  $10 \circ C \cdot \min^{-1}$  under argon atmospheric condition. The start of thermal decomposition was identified when the first exothermic step was observed.

## Thermal stability

DSC measurements were carried out to investigate the thermal stability of the coumarin based iodonium salts. Fig. 10 shows the change in heat flow upon heating of these salts without any additional component. The onset point of heat evolution in the exothermic peak was defined as the initial temperature (Ti) of the compound's decomposition. The neat photoinitiators based on coumarin chromophore were stable up to 170°C, (Figure S57 and Table). Above this temperature, decomposition of the iodonium salts was observed in the DSC. The decomposition of the investigated iodonium salts is shown by the release of heat, resulting in the initiator's thermal decomposition.

Photoinitator	The initial temperature (Ti) of the compound's decomposition	The maximum temperature (Tmax) of the compound's decomposition
7-MP	182,3 °C	194,1 °C
7-M-CN-P	208.0 °C	213.6 °C
7-M-NO <sub>2</sub> -P	178.0 °C	195.3 °C
7-M-Me-P	186.2 °C	198.9 °C
7-M-iPr-P	173.6 °C	193.9 °C





#### 11. The solubility of the coumarin based iodonium photoinitiators

The exactly measured amount (100 mg) of the coumarin based iodonium photoinitiators were transferred into 1 g monomer resulting in a saturated solution containing non-dissolved parts of the initiator. This solution was taken in an ultrasonic bath for 10 minutes in the temperature at 22°C, after that centrifuged to separate non-dissolved iodonium salt. The solution obtained was finally filtrated (it was used the 0.2  $\mu$ m syringe filter) to separate possibly available solid initiator stuff. Some volume (50–100 mg depending on initiator dissolution) of this solution was diluted with 10 ml acetonitrile. Subsequently, UV-Vis measurement was taken from this solution in a quartz cuvette (d = 10 mm), resulting in quantitative information regarding the dissolved initiator in the monomer using the initiator's extinction coefficient in acetonitrile.

Photoinitator	The solubilities of the coumarin based iodonium photoinitiators in the OXT-221 monomer [gdm <sup>-3</sup> ]
7-MP	10,0 [gdm <sup>-3</sup> ]
7-M-CN-P	9,2 [gdm <sup>-3</sup> ]
7-M-NO <sub>2</sub> -P	6,3 [gdm <sup>-3</sup> ]
7-M-Me-P	8,5 [gdm <sup>-3</sup> ]
7-M-iPr-P	4,1 [gdm <sup>-3</sup> ]

12. 3D printing experiment using the direct visible light induced cationic coumarin-based photoinitiators



**Photo.1.** The pattern obtained after the 3D printing experiment based on formulation 7M-P (1% w/w)/ TMPTA/EPOX, characterized by numerical optical microscopy. A 3D printer using a laser diode at 405 nm (size of the spot around 50 μm) with the intensity of 100 mW was used for the spatially controlled irradiation.





**Photo.2.** The pattern obtained after the 3D printing experiment based on formulation 7M-P (1% w/w)/ TMPTA/TEGDVE, characterized by numerical optical microscopy. A 3D printer using a laser diode at 405 nm (size of the spot around 50 μm) with the intensity of 100 mW was used for the spatially controlled irradiation.



**Photo.3.** The pattern obtained after the 3D printing experiment based on formulation: 7M-P (1% w/w)/ TMPTA/TEGDVE, characterized by numerical optical microscopy. A 3D printer using a laser diode at 405 nm (size of the spot around 50 μm) with the intensity of 100 mW was used for the spatially controlled irradiation.



**Photo.4.** The pattern obtained after the 3D printing experiment based on formulation 7M-Me-P(1% w/w)/TMPTA/EPOX, characterized by numerical optical microscopy. A 3D printer using a laser diode at 405 nm (size of the spot around 50 μm) with the intensity of 100 mW was used for the spatially controlled irradiation.



Photo.5. The pattern obtained after the 3D printing experiment based on formulation 7M-iPr-P(1% w/w)/TMPTA/EPOX, characterized by numerical optical microscopy



**Photo.6.** The pattern obtained after the 3D printing experiment based on formulation 7M-iPr-P(1% w/w)/TMPTA/EPOX, characterized by numerical optical microscopy. A 3D printer using a laser diode at 405 nm (size of the spot around 50 μm) with the intensity of 100 mW was used for the spatially controlled irradiation.

<sup>1</sup> Pol. Pat. Appl. P-393 501 2010. Pol. Pat. Appl. P-395 515 2011.