Supporting Information

2,4,6-Trimethylbenzoyldiphenylphosphine Oxide (TPO) Analog: A Non-Cytotoxic Type-I Photoinitiator for Free Radical Photopolymerization

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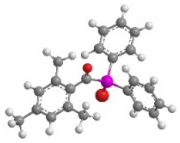
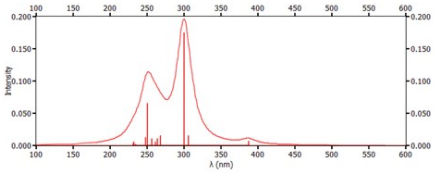
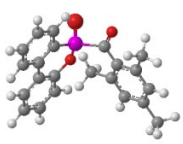
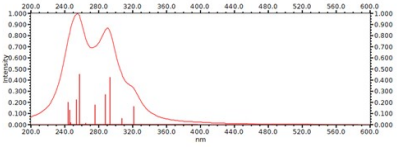
Table S1
Theoretical calculations method used (B3LYP/6-31G*)

Optimized structures	BDE (kcal mol^{-1})	E_T (kcal mol^{-1})	Spectra UV-vis
 TPO	55.0	54.8	 (100 nm < λ < 600 nm) λ_{max}= 300 nm F= 0.176 λ_{max}= 251 nm F= 0.066 λ_{max}= 306 nm F= 0.016 λ_{max}= 388 nm F= 0.008
 TDOPO	54.26	56.40	 (100 nm <λ < 600 nm) λ_{max}= 294 nm F= 0.1338 λ_{max}= 258 nm F= 0.1421 λ_{max}= 397 nm F= 0.0010

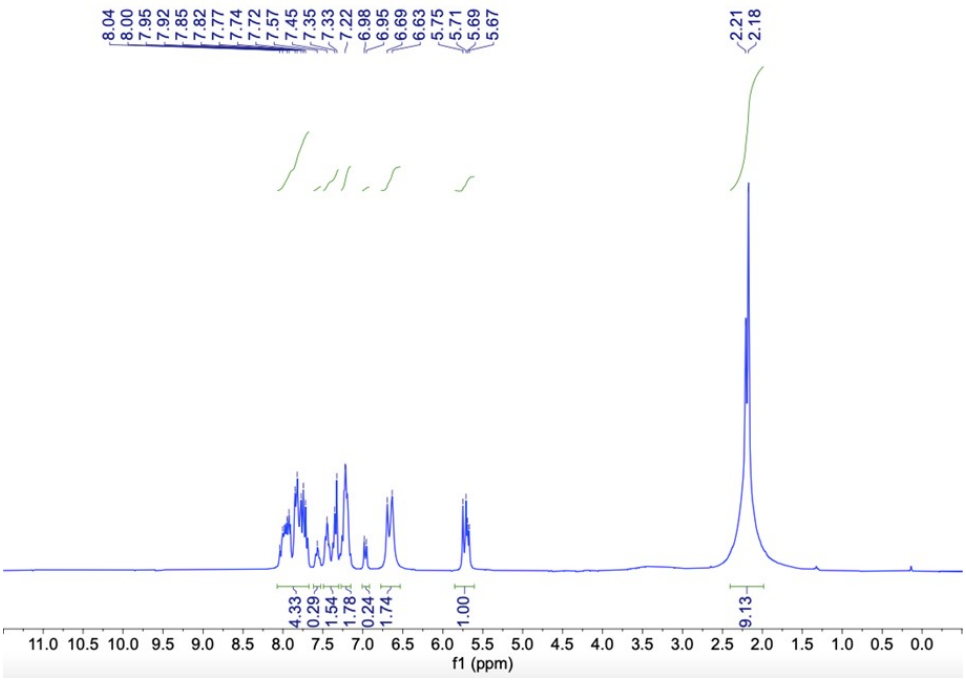


Figure S1. ^{1}H-NMR spectrum of Alc-1.

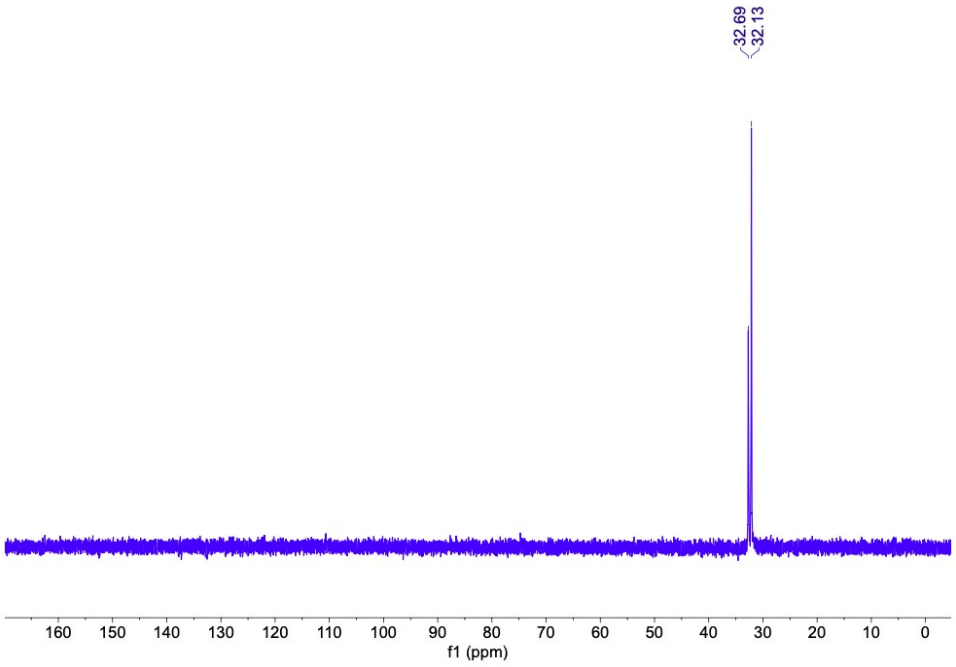


Figure S2. ^{31}P-NMR spectrum of Alc-1.

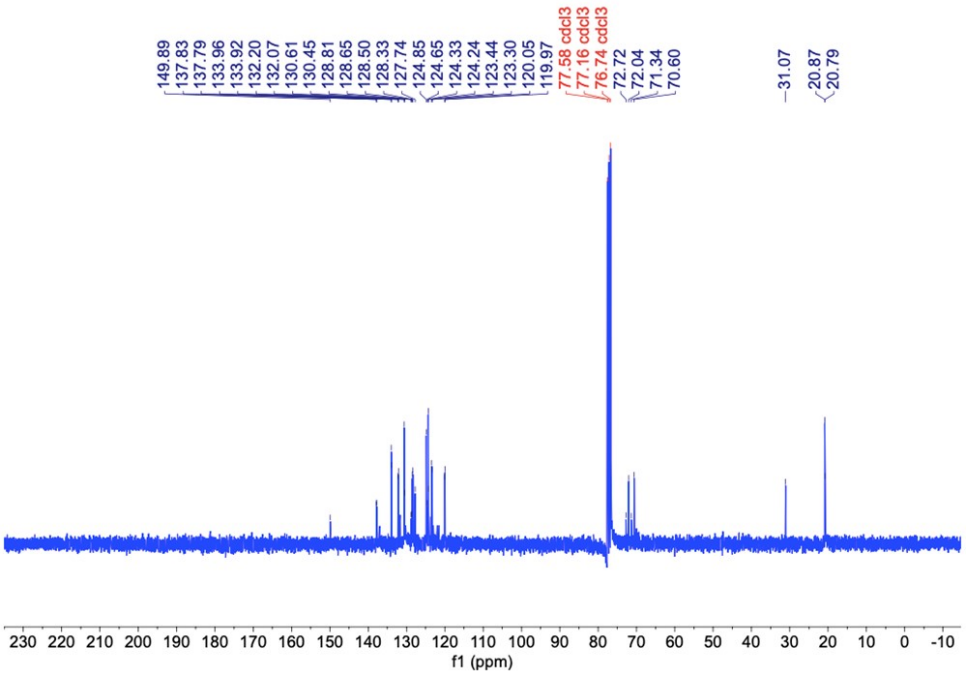


Figure S3. ^{13}C-NMR spectrum of Alc-1.

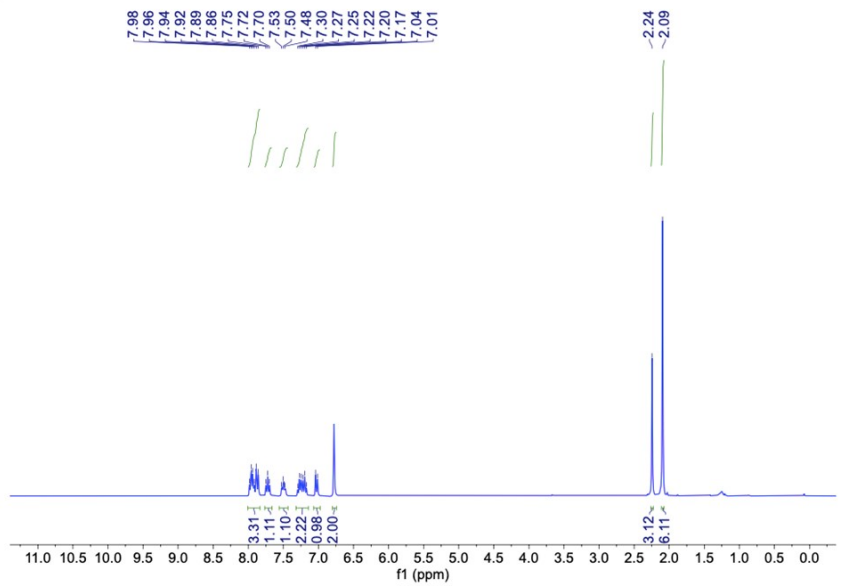


Figure S4. ^{1}H-NMR spectrum of the freshly synthesized TDOPO.

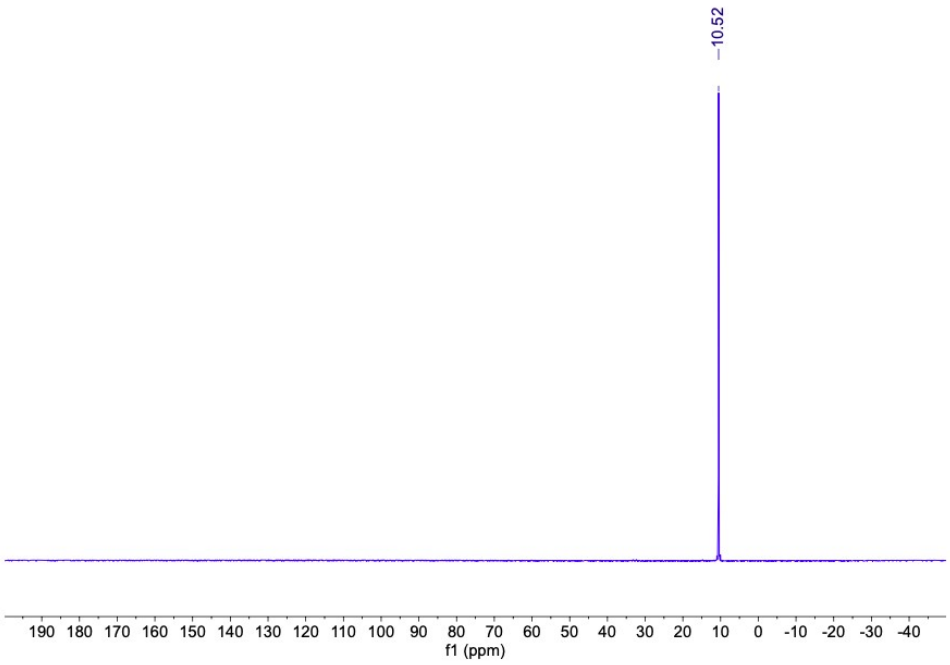


Figure S5. ^{31}P-NMR spectrum of TDOPO.

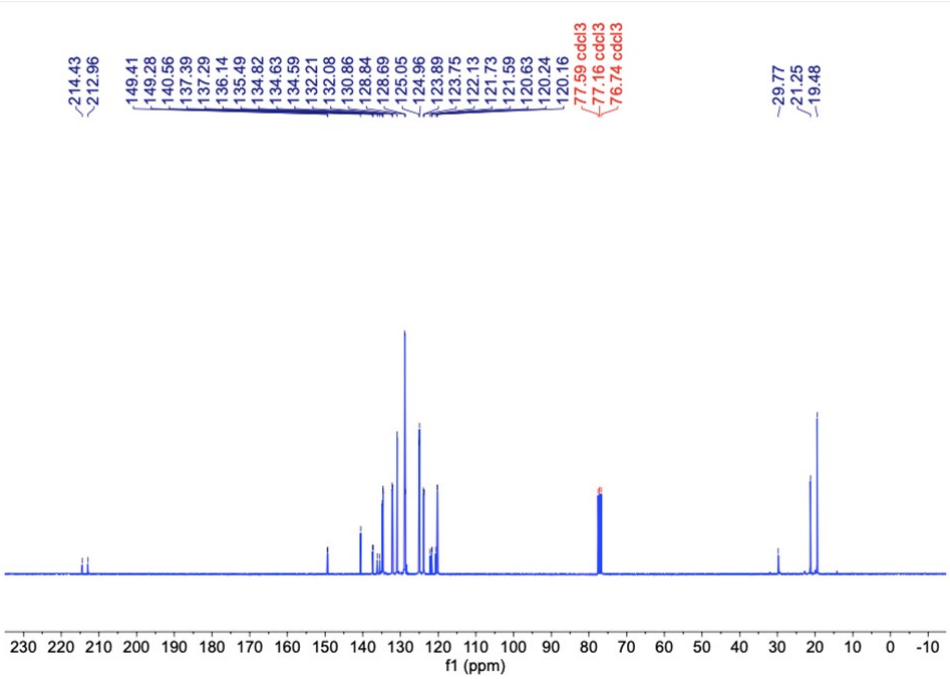
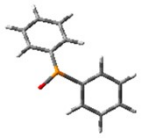


Figure S6. ^{13}C-NMR spectrum of TDOPO.

Spin density P: 0.492010
Spin density O: 0.259310

Spin density C : 0.646268

Figure S7. The parameter evaluated is the spin density around the formed radicals (P•, C• and O•) for TDOPO.



Spin density on P 0.481521

Figure S8. The parameter evaluated is the spin density around the formed radicals (P•) for TPO.

Storage stability of the synthesized photoinitiator

Figure S4 shows the ^{1}H NMR spectrum of the freshly synthesized TDOPO, and Figure S9 shows the ^{1}H NMR spectra of the prepared TDOPO after it was sealed in the dark for three months, and the spectra did not change significantly.

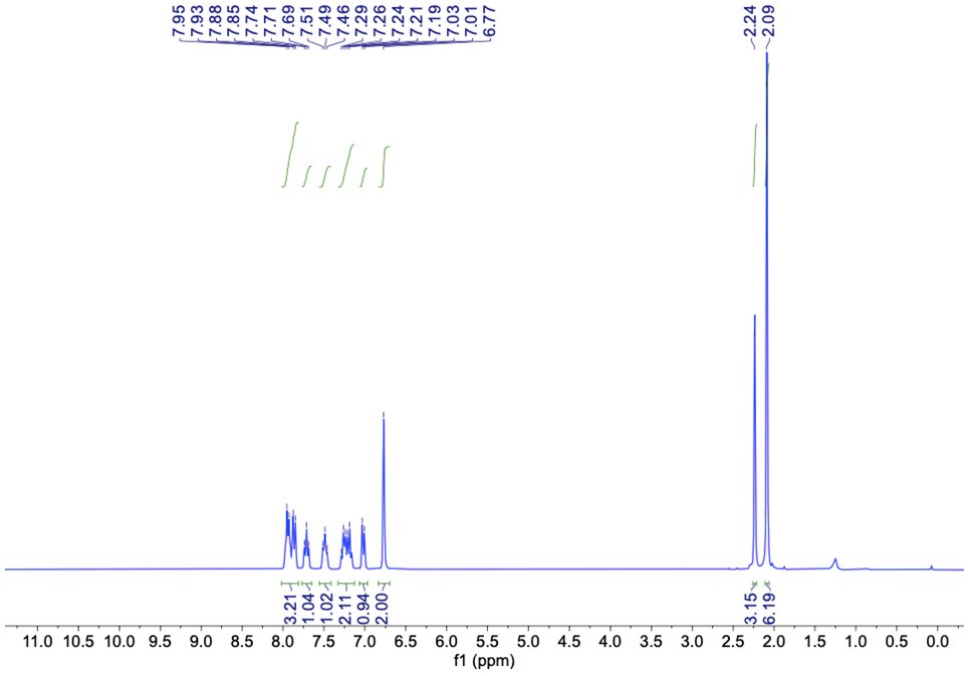


Figure S9. ^{1}H-NMR spectrum of the prepared TDOPO after it was sealed and protected from light for three months.

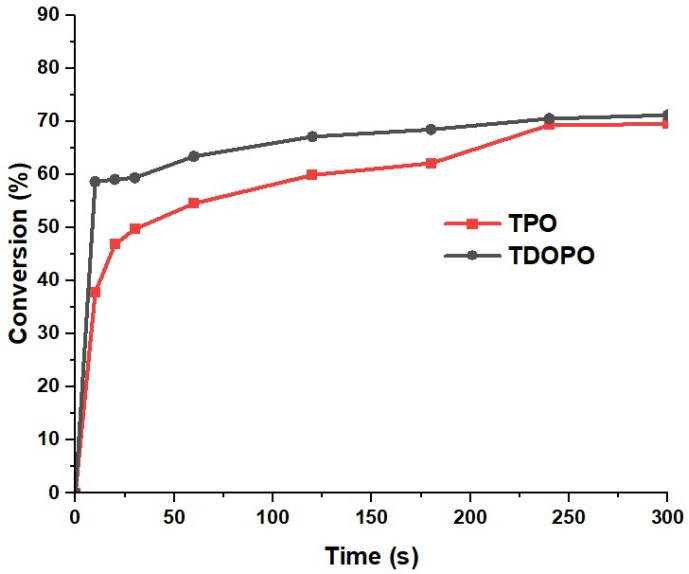


Figure S10. Photopolymerization profiles of TMPTA thick sample (acrylate functions conversion vs. time) thickness = 2 mm, under air, using sunlight (Mulhouse, eastern France, summer, temperature 26 °C). 2.80×10^{-5}mol·g$^{-1}_{TMPTA}$ TDOPO compared with 2.80×10^{-5}mol·g$^{-1}_{TMPTA}$ TPO

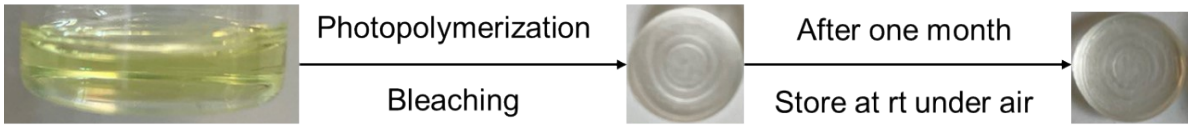


Figure S11. Photopolymerization experiments were conducted with a TDOPO concentration of 2.80×10^{-5} mol·g$^{-1}_{TMPTA}$. The image on the left shows unpolymerized TMPTA, the middle image displays TMPTA after polymerization, and the image on the right depicts TMPTA one month after polymerization.

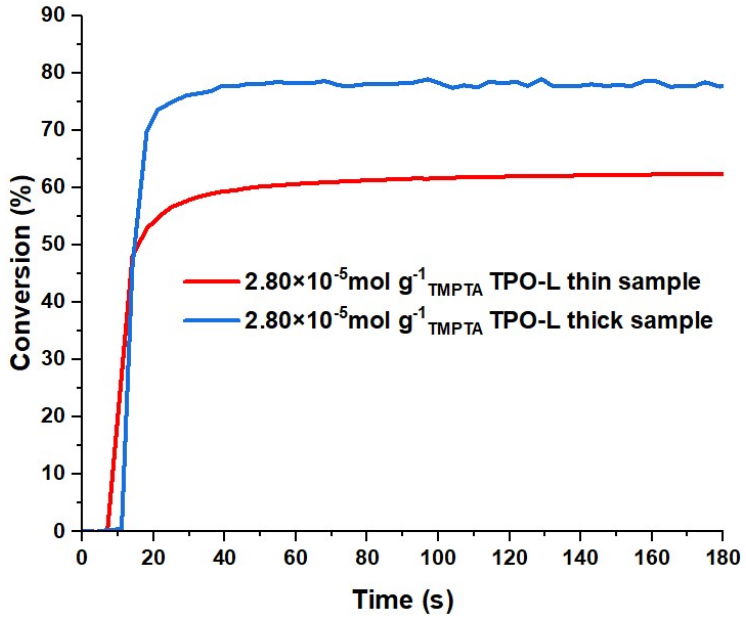


Figure S12. Photopolymerization profiles of TMPTA thick sample (acrylate functions conversion vs. time) thickness = 2 mm and thin sample = 25 µm, under air, using LED@405nm (100 mW/cm^2), irradiation starts at t = 10 s. Concentration = 2.80×10^{-5}mol·g^{-1}$_{TMPTA}$ TPO-L. The red curve represents the thin sample, the blue curve represents the thick sample.

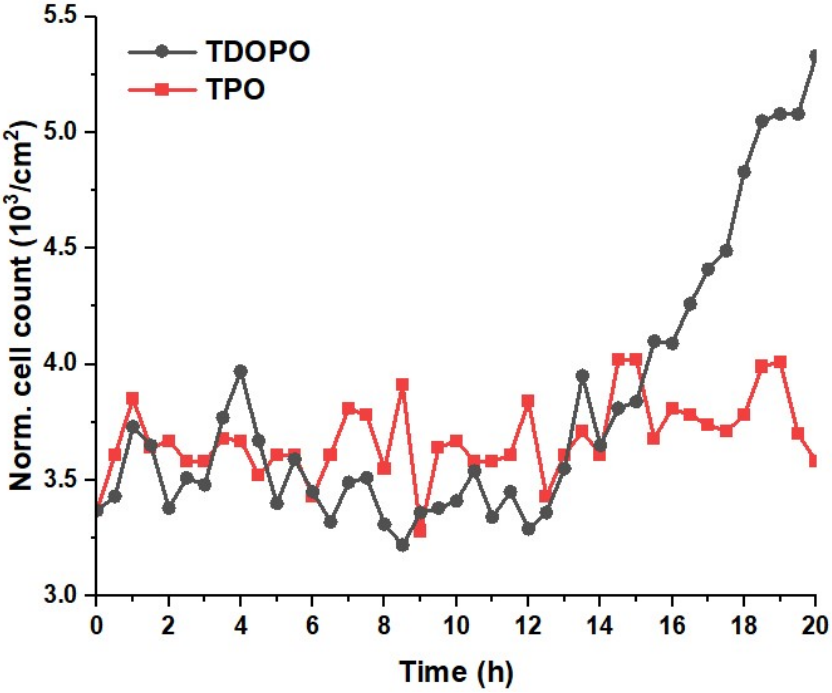


Figure S13. Number of cells per well standardized results.

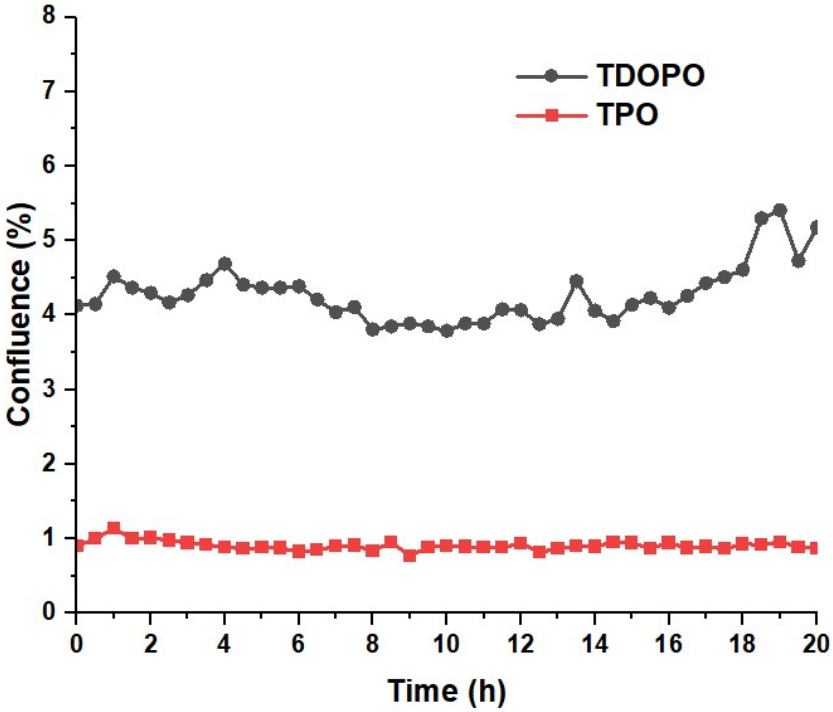


Figure S14. Confluences of cells per well.

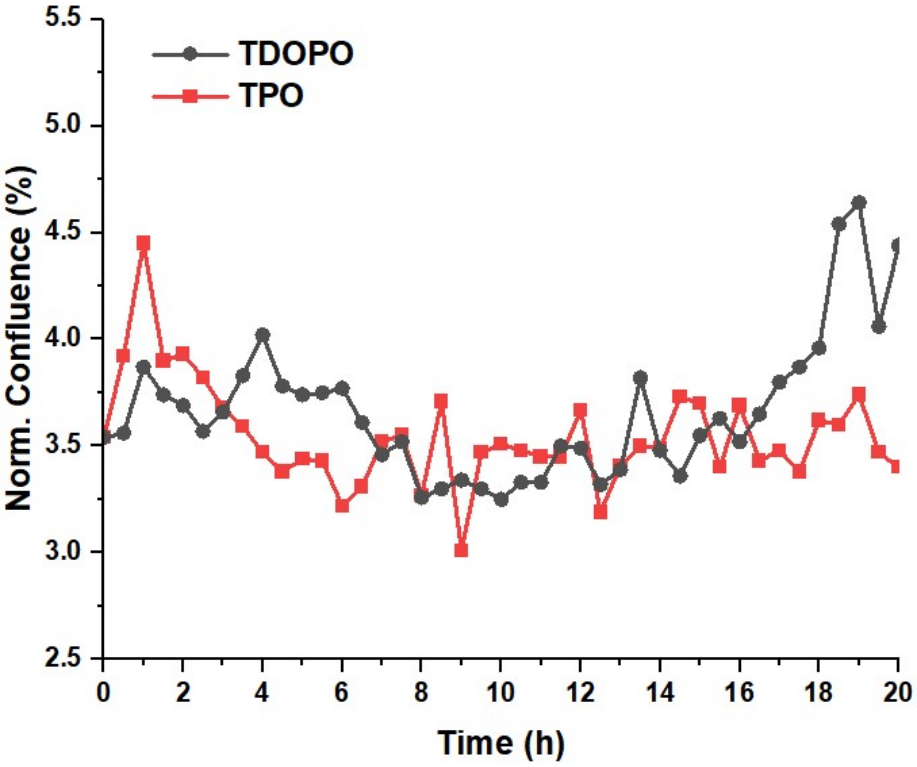


Figure S15. Confluences of cells per well standardized results.

Cytotoxicity testing of photodegradation and photopolymerization products

Sample prepararation:

TPO photopolymerization products (TPO POLY) and TDOPO photopolymerization products

(TDOPO POLY) were prepared by 1 g of TMPTA at 2.80×10^{-5}mol·g^{-1} TMPTA concentration of TPO and TDOPO after ten seconds of illumination at 405 nm. TPO photodegradation products (TPO PP) and TDOPO photodegradation products (TDOPO PP) were prepared by dissolving TPO and TDOPO in DMSO solution respectively to form a 50 mM concentration solution and then irradiated at 405 nm for 10 min.

The samples were placed in a complete medium according to the international standard ISO 10993-12. The surfaces were incubated for 24 hours at 37°C and 5% CO2. The test was performed on C3H10 T1/2 cell lines seeded the day before in 24-well plates at 104 cells/well. The medium was then replaced with the medium containing the released molecules.

After 24 hours of incubation, the AlamarBlue (Thermofisher) cytotoxicity test was performed according to the supplied instructions. The results were read with the fluorescence spectrometer (JASCO FP-750) at 590 nm excitation wavelength and expressed as a percentage of cell viability.

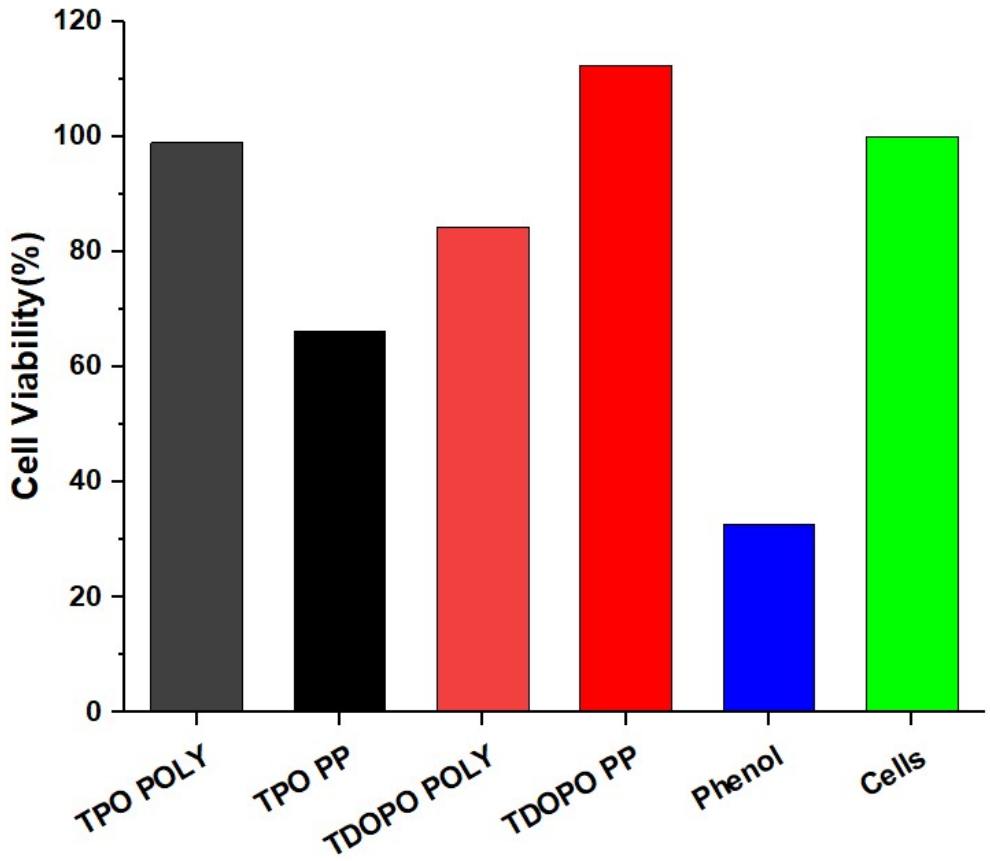
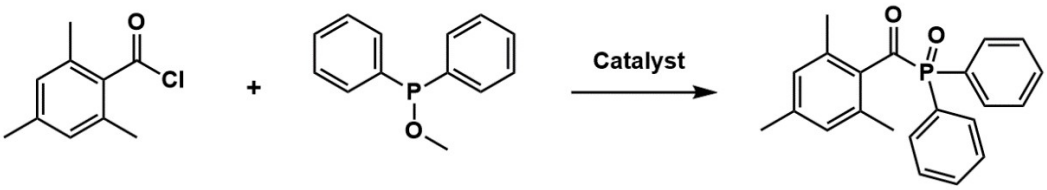


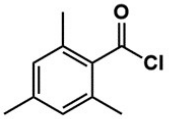
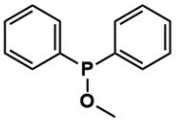
Figure S16. Cytotoxicity testing of TPO POLY, TDOPO POLY, and TPO PP versus TDOPO PP. There was a cytotoxicity control phenol as well as a blank control Cell

Table S2

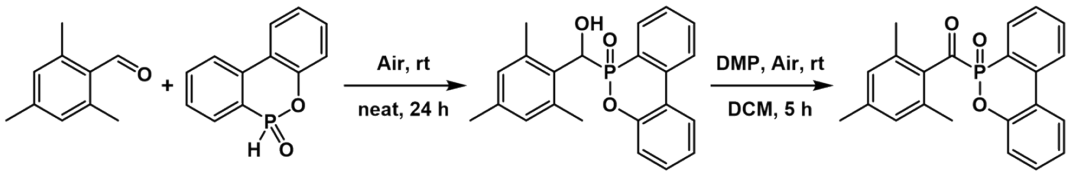
Cost comparison between industrial synthetic TPO and laboratory synthetic TDOPO

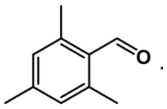
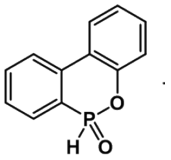
TPO industrial production process (main industrial production process)



Reactant	Prices (€/g)	Supplier
	0.55	TCI
	17.6	TCI
Total Price	18.15	

TDOPO synthesis route



Reactant	Prices (€/g)	Supplier
	2.88	TCI
	0.21	TCI
Total Price	3.09	