## **Supporting Information**

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Title:

Synthesis and testing of ZnO nanoparticles for photo-initiation: Observation of two

different non-migration initiators for bulk polymerization

## **Section Tables**

*Table S1*. Summary of the relevant vibrational bands in Figure 1. For details, refer to textbooks, such as that by G. Socrates<sup>35</sup>.

range [cm <sup>-1</sup> ]	Vibration
3550-3230	OH stretching vibration
2975-2950	CH <sub>3</sub> asym. stretching vibration
2885-2865	CH <sub>3</sub> sym. stretching vibration
2930	CH <sub>2</sub> asym. stretching vibration
2870-2840	CH <sub>2</sub> sym. stretching vibration
1650-1550	COO <sup>-</sup> asym. stretching vibration
1440-1360	COO <sup>-</sup> sym. stretching vibration
1720-1700	C=O stretching vibration
≈ 1500	vibration bands of ZnO like adsorbed X-OH vibrations
1050	C-O stretching vibrations

## Section Figures; Synthesis and Experimental:



Figure S1: An image of the centrifuge beaker directly after the first step of the synthesis clearly shows the separation of the ZnO-rich (upper layer) from the NaCl-rich phase (lower layer) due to the differences in precipitation rate during centrifugation.



Figure S2: XRD diffraction pattern of nanoparticulate ZnO:Cu(II) (1 mol%) without baseline correction. The small increase in the baseline can be interpreted as resulting from a small amount of amorphous material.



Figure S3: Spectral irradiation correction used to calibrate the fiber-optical receiver. For details of the procedure, refer to Schmitt and Heib  $(2014)^{66}$ .



Figure S4: Visualization contrasting manual measurement of the Raman experiment with the automatically performed experiment. The relative double bond content of the C=C aromatic and the C=O vibration bands are presented.



Figure S5: *Real time* UV-vis measurement, sensitive to area solidification for wavelengths below or within the absorbance of the initiator. On the left-hand side, changes during the solidification using Irgacure® 2959 are presented. On the right-hand side, changes during the solidification of  $ZnO:Pt^{II}$  are presented. For the calculation of the values presented in Table 2, the results of nine spectra were averaged. It is clearly observed that the area solidification with light < 300 nm was much faster for the molecular initiator.



Figure S6: *In situ* UV-vis measurement during the precipitation of  $ZnO:Mn^{II}$  (1.6 mol%). After 3 s, the clouding was too pronounced for data acquisition using this setup (2 x 1-mm thickness). The formation of the ZnO can be clearly detected by its bandgap. The limit in growth appears to have been achieved (Figure S7).



Figure S7: UV-vis spectrum of the  $ZnO:Mn^{II}$  (1.6 mol%) supernatant obtained after synthesis, along with spectra recorded during the synthesis.



Figure S8: Image of a 0.5 mm cured layer; sample acrylic ester resin cured by 20 wt% of the paste containing  $ZnO:MnCl_2$  (0.5 mol%) and a 500 W continuous xenon-arc lamp (approximately 5 min of illumination).<sup>29</sup>



Figure S9: Image of a 0.5 mm cured layer; sample acrylic ester resin cured by 20 wt% of the paste containing  $ZnO:MnCl_2$  (1.6 mol%) and a 500 W continuous xenon-arc lamp (approximately 5 min of illumination).<sup>29</sup>



Figure S10: Image of a 0.5 mm cured layer; sample acrylic ester resin cured by 20 wt% of the paste containing  $ZnO:MnCl_2$  (2.1 mol%) and a 500 W continuous xenon-arc lamp (approximately 5 min of illumination).<sup>29</sup>

Section Figures; ESR:



Figure S11: Signal resulting from irradiation of the acrylic mixture <sup>29</sup> with 20 wt% of the paste containing ZnO:Cu<sup>II</sup> (1 mol%). The blue arrow indicate the typical Cu(II) signal, which decreases with irradiation. The green arrow indicates the signal from the mid-chain radical. The red arrow indicates the signal from the trapped electron. Note that the modulation of the *B*-field is alternated (scaling by 0.78 is necessary). Measurements were performed in the dark, and the irradiation was passed through a 6 mm high-pass filter (320 nm).



Figure S12: ESR spectra after the irradiation of ZnO:benzoyl formic acid in an acrylic mixture (20 wt% of paste). The arrows indicate the typical signals from the mid-chain radical with a singlet "very immobile region" (black) and a triplet "cured" (red) and from the trapped electron within the ZnO (green). The signal of the mid-chain radical in the immobile region is stronger than that of the radical cured using classical initiators (Figure S13). Measurements were performed in the dark, and the irradiation was passed through a 6 mm high-pass filter (320 nm). Superposition of the signal with the electron vacancies was possible.



Figure S13: ESR signals from the mid-chain radical cured by commercial initiators (2 wt%) after irradiation cycle  $2^{29}$ . The relative signal of the mid-chain radical in the immobile region is not as strong as that of the radical cured using nanoparticle initiators (Figure S12).



Figure S14: Size distribution of the ZnO:levulinic acid (>8.5 mol%) sample (Figure S22). From the variation in the diameter, resulting in no maximum (>0 nm), it can be assumed that the particles were spherical. The number of measured (smallest and largest diameter) particles was 536.



Figure S15: TEM image of a sample from the ZnO:Cu(II) (1 mol%) paste. Primary crystallites can be observed.



Figure S16: TEM image of a sample from the ZnO:Cu(II) (2 mol%) paste. Primary crystallites can be observed.



Figure S17: TEM image of a sample from the ZnO:Mn(II) (0.5 mol%) paste. Manganese (EDX, top) and primary crystallites can be observed. The content of Mn, determined by EDX, is 0.31 mol%.



Figure S18: TEM image of a sample from the ZnO:Mn(II) (1.6 mol%) paste. Manganese (EDX, top) and primary crystallites and aggregations can be observed. The content of Mn by EDX is 0.98 mol%.



Figure S19: TEM image of a sample from the ZnO:Mn(II) (2.2 mol%) paste. Manganese (EDX, top) and primary crystallites can be observed. The content of Mn by EDX is 1.36 mol%.



Figure S20: TEM image of a sample from the ZnO:Pt(II) (0.7 mol%) paste. Platinum (EDX, top) and primary crystallites can be observed. The content of Pt by EXD is 0.46 mol%.



Figure S21: TEM image of a sample from the ZnO:Pt(0) (0.7 mol%) paste. Platinum (EDX, top) can be observed. More aggregation is apparent than in the other samples. The content of Pt by EXD is 0.31 mol%.



Figure S22: TEM image of a sample from the ZnO:levulinic acid (> 8.5 mol%) paste. Dispersion is very good.



Figure S23: TEM image of a sample from the ZnO:levulinic acid (17 mol%) paste. Primary crystallites can be observed.