Supporting Information for

In-situ Production of Visible Light Absorbing Ti-based Nanoparticles in Solution and in a Photopolymerizable Cationic Matrix.

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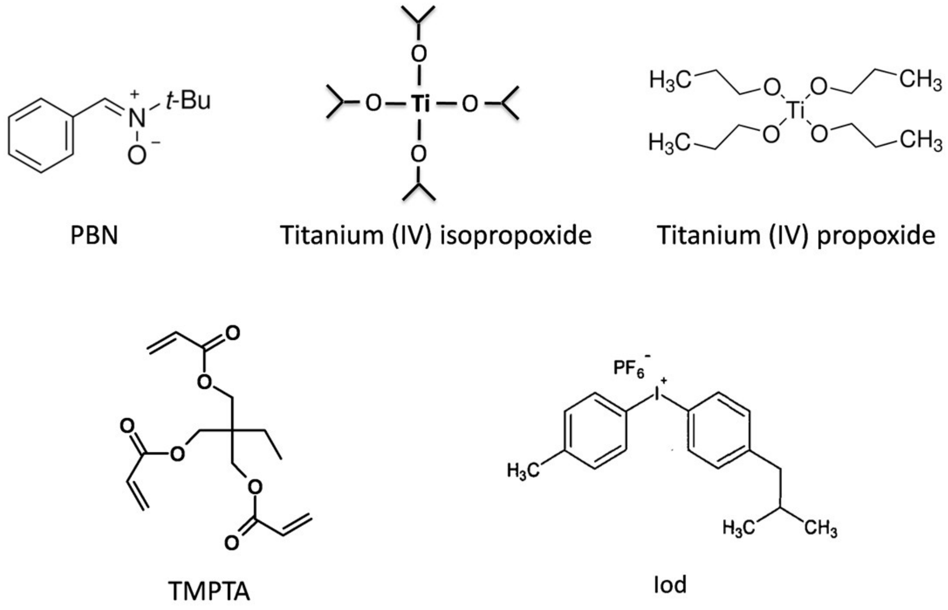
Experimental section

Materials

The compounds presented in Scheme S1 are used with the best purity availaible. N-*tert*-Butyl-α-phenylnitrone (PBN), titanium (IV) isopropoxide (TiOx1) and titanium (IV) propoxide (TiOx2) were respectively purchased from Aldrich; (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) was obtained from Allnex and used as benchmark monomer for cationic photopolymerization. Trimethylolpropane triacrylate (TMPTA) and the iodonium salt ((4-methylphenyl)[4-(2-methylpropyl) phenyl]- hexafluorophosphate; Iod) were kindly provided by Sartomer and BASF company, respectively.

Scheme 1. Investigated compounds



Methods

ESR Spin Trapping (ESR-ST) Experiments. The ESR experiments were carried out using a X-Band spectrometer (MS 400 from Magnettech-Berlin, Berlin, Germany) at room temperature (293K). The radicals were generated under aerated and argon atmosphere at room temperature using polychromatic light irradiation (Xe-Hg lamp; Hamamatsu, L8252, 150 W) and trapped by phenyl-N-tertbutylnitrone (PBN) according to a procedure described in detail in 1. The ESR spectra simulations were generated using the PEST WINSIM program. All of the samples were prepared in a 6 mm quartz cylindrical tube and dissolved in tert-butylbenzene as an inert solvent.

UV-Vis Spectroscopy. UV spectra were recorded on a Varian spectrophotometer (Cary 50 bio).

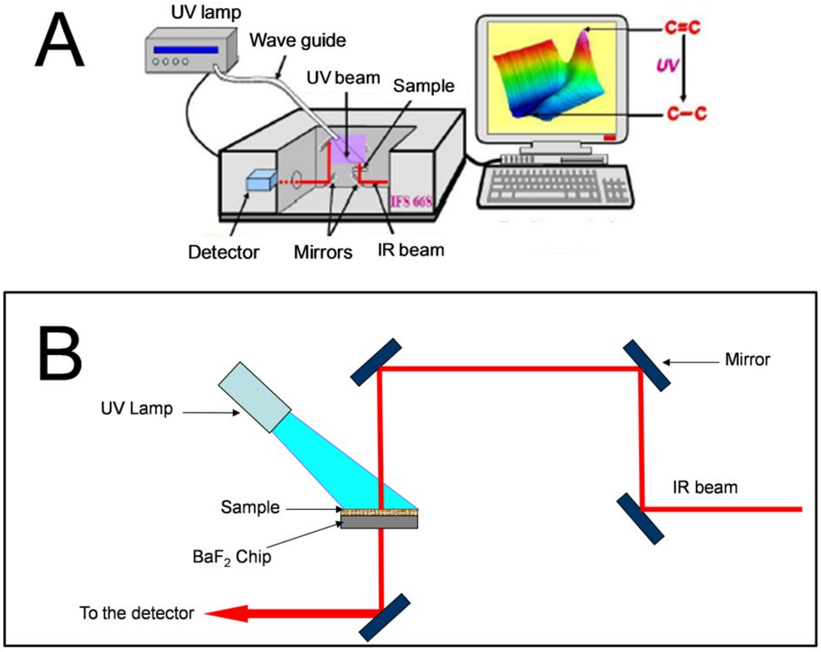
Transmission Electron Microscopy (TEM). Observations were conducted on a Tecnai F20 ST microscope (field-emission gun operated at 3.8 kV extraction voltage) operating at an acceleration voltage of 200 kV and equipped with a X-ray energy-dispersive spectrometer (XEDS from Oxford Instruments) for chemical analysis. The samples were prepared as follow: a 15 µL drop of toluene nanoparticle suspension was deposited on a carbon coated 400 mesh copper grid. Once the toluene evaporated at room temperature, it left a distribution of particles on the support film.

Transmission Electron Microscopy for polymer films analysis. Observations were conducted on a Philips CM200 microscope operating at an acceleration voltage of 200 kV. For metal nanoparticles embedded in a polymer matrix, slides of 70 nm were analyzed (microtome Leica, EM UC7).

Cationic Polymerization Processes. The one and two-component photoinitiating systems are based on Iod (3 wt%), TiOx1/Iod (1% / 3% w/w) and TiOx2/Iod (1% / 3% w/w), respectively. The experimental conditions are given in the corresponding figure captions. Kinetics of photopolymerization were followed by Real Time Fourier Transform InfraRed Spectroscopy (RT-FTIR) using a JASCO instrument. The liquid samples were applied to a BaF2 pellet by means of calibrated wire-wound applicator. The film thickness was evaluated at 25µm in the photocuring experiments. The RT-FTIR analyses were carried out under air conditions. Samples were simultaneously exposed to both UV beam, which starts the photopolymerization, and the IR beam which analyzes the extent of the photoreaction in-situ. Samples were irradiated during 400s at room temperature, by means of a Lightningcure LC8 (L8251) from Hamamatsu, equipped with a mercury-xenon lamp (polychromatic light, $\lambda >$ 300nm) coupled with a flexible light guide. The maximum UV light intensity at the sample position was evaluated to be 80mW/cm^2. The photopolymerization was monitored by the disappearance of the epoxy function of the EPOX monomer at 790 cm^{-1}.

Free Radical Polymerization Processes. The one and two-component photoinitiating systems are based on Iod (3 wt%), TiOx1/ Iod (1% / 3% w/w) and TiOx2/ Iod (1% / 3% w/w), respectively. The experimental conditions are given in the corresponding figure captions. Kinetics of photopolymerization were followed by Real Time Fourier Transform InfraRed Spectroscopy (RT-FTIR) using a Thermo-Nicolet 6700 instrument. The liquid samples were applied to a BaF_2 pellet by means of calibrated wire-wound applicator. The film thickness was evaluated at 4µm in the photocuring experiments. Samples were irradiated during 360s at room temperature, by means of a Lightningcure LC8 (L8251) from Hamamatsu, equipped with a mercury-xenon lamp (polychromatic light, $250 < \lambda < 800$nm) coupled with a flexible light guide. The maximum UV light intensity at the sample position was evaluated to be 200 mW/cm^2. The photopolymerization was monitored by the disappearance of the acrylate function of the TMPTA monomer at 1636 cm^{-1}. RT-FTIR experimental set-up is displayed in Scheme 2.

Scheme 2. RT-FTIR experimental set-up: A) Schematic representation of the IR spectrometer and B) zoom on the sample compartment



Density Functional Theory Calculations. Input structures were generated with Avogadro program and subsequently optimized by means of DFT calculations with the Gaussian09 package. Computations were conducted by means of the M06 functionals along with the LANL2DZ basis sets and pseudo-potentials for Ti atoms and the Pople style basis 6-31G(d,p). Additional checks were conducted with M06-L functional and LANL2TZ+ basis set for Ti and 6-31+G(d,p). The frequencies computed at each optimized structure reveal all real, verifying they are a minimum of the Potential Energy Surface (PES). Thermochemistry predictions were calculated at 298K based on the harmonic approximations by means of the aforementioned frequency calculations.

Experimental Results

Figure S1.

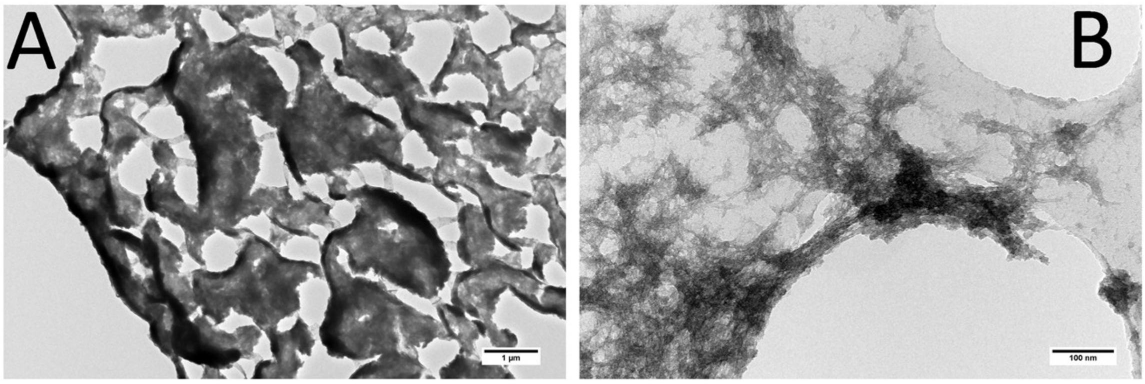


Figure S1. TEM images of the photolysis of titanium oxide complexes alone: A) titanium (IV) propoxide (TiOx2) after 360s of irradiation and B) titanium (IV) isopropoxide (TiOx1) after 360s of irradiation in dry toluene. Hg-Xe lamp exposure at room temperature (polychromatic light, 250 nm < λ < 800 nm). Under air. [TiOx1] = [TiOx2] = 2.7×10^{-2}M

Figure S2

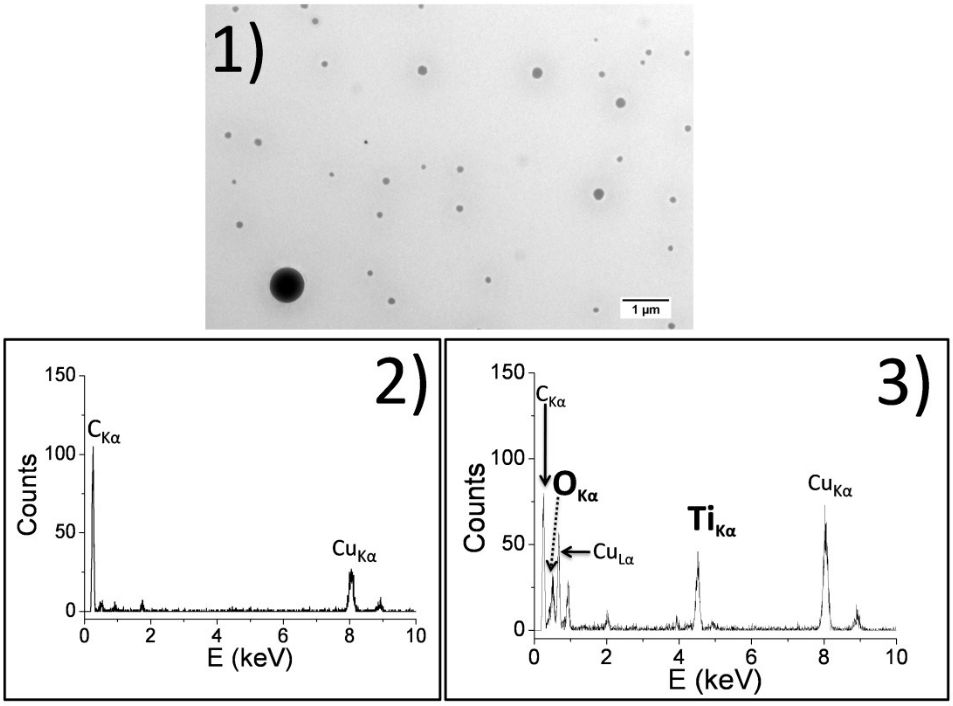


Figure S2. 1) TEM image of the photoinduced titanium-based nanoparticles from the photolysis of the titanium (IV) propoxide (TiOx2)/ Iod system after 360s of irradiation in dry toluene, 2) EDX spectra acquired in STEM with the same exposure time on the supporting membrane and 3) on a single titanium-based nanoparticle. Hg-Xe lamp exposure at room temperature (polychromatic light, 250 nm < λ < 800 nm). Under air. [TiOx2] = 2.7x10^{-2} M, [Iod] = 2.5x10^{-2} M.

Figure S3.

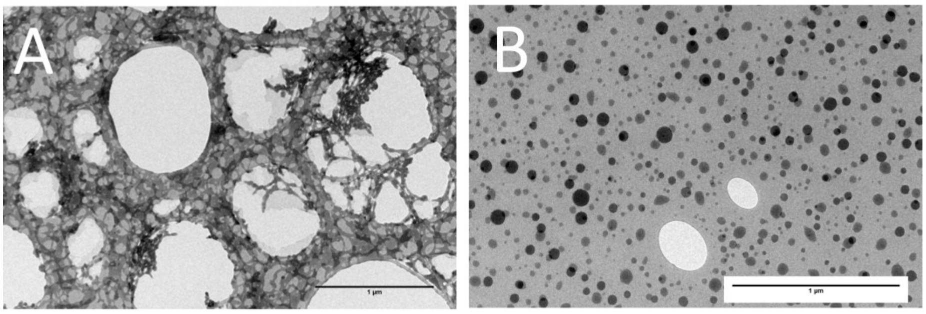


Figure S3. TEM images of the photoinduced titanium-based nanoparticles from the photolysis of TiOx2/Iod in propan-2-ol (A and B). Xe-Hg lamp exposure at room temperature (polychromatic light, 250 nm < λ < 800 nm). 360s of irradiation. Under air. [TiOx2] = 2.9×10^{-2} M, [Iod] = 3.2×10^{-2} M.

Figure S4.

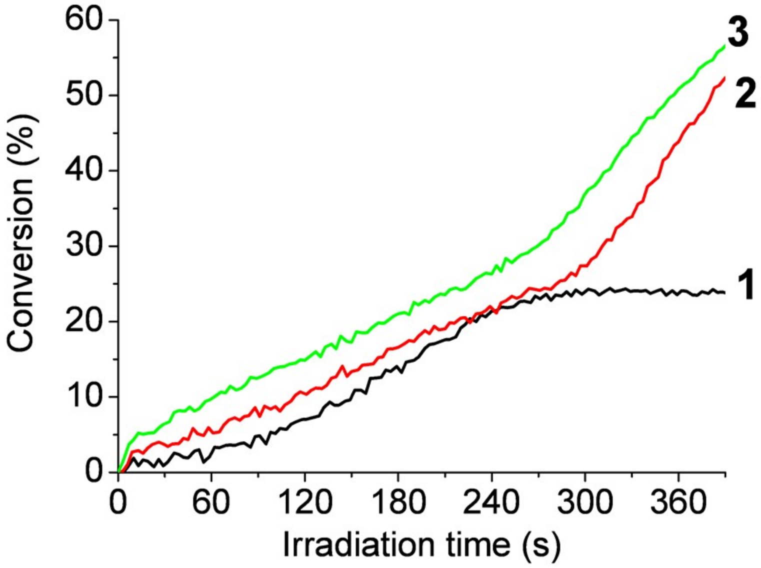


Figure S4. Photopolymerization profiles of TMPTA. Photoinitiating systems: 1) Iod (3wt%), 2) TiOx1 (1wt%)/Iod (3wt%) and 3) TiOx2 (1wt%)/Iod (3wt%). Xe-Hg lamp exposure (polychromatic light at λ > 300nm). Under air.

Figure S5.

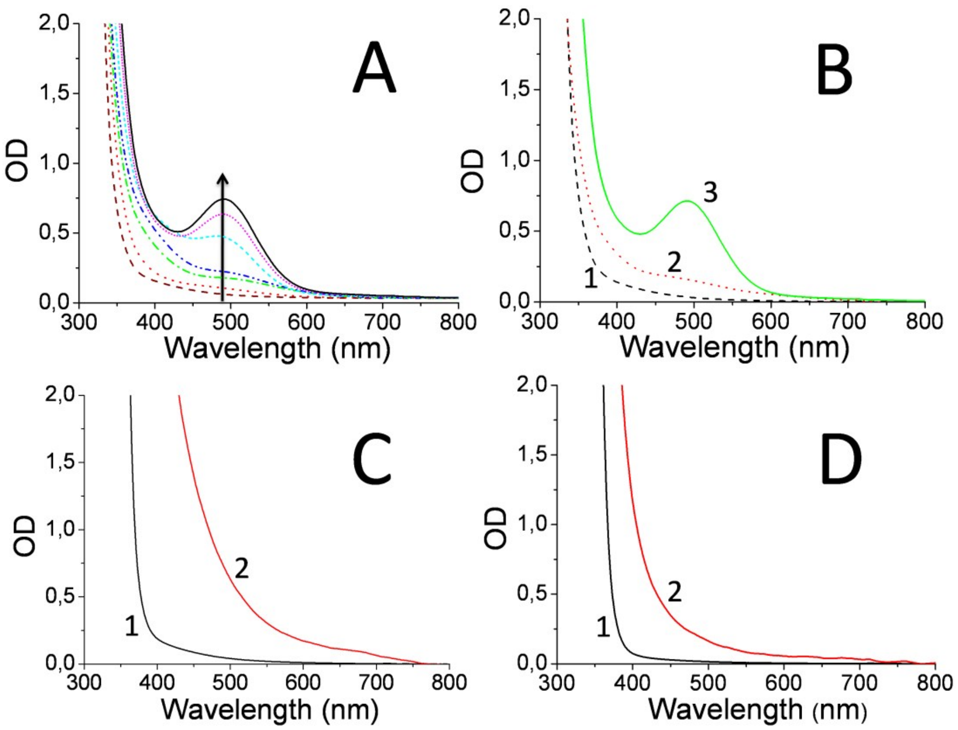


Figure S5. A) Photolysis of the titanium (IV) propoxide (TiOx2)/ Iod system in aerated conditions during 360s of irradiation; B) Effect of the atmosphere on the photolysis of the titanium (IV) propoxide/ Iod system under UV irradiation after 1) 0s, 2) 360s under argon atmosphere and 3) 360s in aerated conditions; C) Photolysis of titanium (IV) propoxide/ Iod /PBN system under UV irradiation in aerated conditions after 1) 0s and 2) 360s; D) Photolysis of Iod/PBN system under UV irradiation in aerated conditions after 1) 0s and 2) 360s. Xenon-Mercury lamp exposure (polychromatic light, 250 nm < λ < 800 nm). Photolysis at room temperature. [TiOx2] = 2.7x10^{-2} M, [Iod] = 2.5x10^{-2} M.

Figure S6.

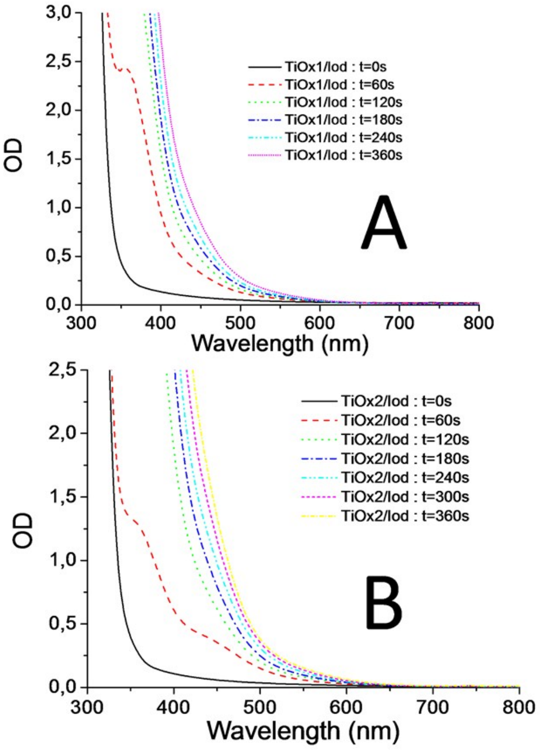


Figure S6. Photolysis of A) the titanium (IV) isopropoxide (TiOx1)/Iod system and B) the titanium (IV) propoxide (TiOx2)/Iod system in aerated conditions in propan-2-ol after 360s of irradiation. Hg-Xe lamp exposure at room temperature (polychromatic light, 250 nm < λ < 800 nm). Under air. [TiOx1] = [TiOx2] = 2.7×10^{-2} M, [Iod] = 2.5×10^{-2} M.

Figure S7.

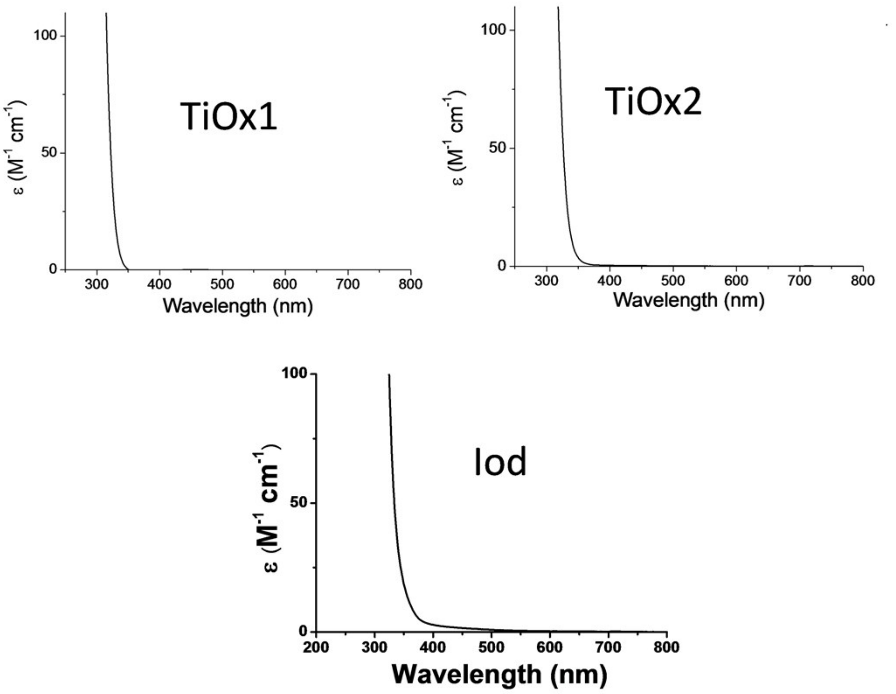


Figure S7. UV absorption spectra of TiOx1, TiOx2 and Iod in dry toluene.