A Well-Define Titanium Complex for Free-Radical and Cationic Photopolymerizations Under Visible Light and Photoinduction of Ti-based Nanoparticles

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Figure S1. Free-radical photopolymerization of TMPTA in the presence of ITX/Trithiol (1% / 3%, w/w) upon 1) LED@385nm (12.5 mW/cm²) under air 2) LED@385nm (12.5 mW/cm²) in laminate, 3) LED@405nm (12.5 mW/cm²) under air, 4) LED@405 nm (12.5 mW/cm²) in laminate, 5) LED@405nm (100 mW/cm²) under air and 6) LED@405nm (100 mW/cm²) in laminate. Thickness = 12 μ m.



Figure S2. Free-radical photopolymerization of TMPTA in the presence of ITX/MDEA (1% / 3.7%, w/w) upon 1) LED@385nm (12.5 mW/cm²) under air 2) LED@385nm (12.5 mW/cm²) in laminate, 3) LED@405nm (12.5 mW/cm²) under air, 4) LED@405 nm (12.5 mW/cm²) in

laminate, 5) LED@405nm (100 mW/cm²) under air and 6) LED@405nm (100 mW/cm²) in laminate. Thickness = 12 μ m.



Figure S3. Free-radical photopolymerization of TMPTA in the presence of 1) Iod/Trithiol (3.7% / 3%, w/w) under air upon LED@385 nm (12.5 mW/cm^2), 2) **TiQ**/Iod/Trithiol (1% / 3.7% / 3%, w/w/w) under air upon LED@385 nm (12.5 mW/cm^2), 3) **TiQ**/Iod (1% / 3.7%, w/w) in laminate upon LED@385 nm (12.5 mW/cm^2), 4) **TiQ**/Iod/Trithiol (1% / 3.7% / 3%, w/w/w) under air upon LED@405 nm (100 mW/cm^2), 5) **TiQ**/Iod (1% / 3.7%, w/w) in laminate upon LED@405 nm (12.5 mW/cm^2), 6) **TiQ**/Iod (1% / 3.7%, w/w) in laminate upon LED@405 nm (12.5 mW/cm^2), 6) **TiQ**/Iod (1% / 3.7%, w/w) in laminate upon LED@405 nm (12.5 mW/cm^2), 6) **TiQ**/Iod (1% / 3.7%, w/w) in laminate upon LED@405 nm (12.5 mW/cm^2), 6) **TiQ**/Iod (1% / 3.7%, w/w) in laminate upon LED@405 nm (100 mW/cm^2), 7) **TiQ**/Iod/Trithiol (1% / 3.7% / 3%, w/w/w) in laminate upon LED@385 nm (12.5 mW/cm^2) and 8) **TiQ**/Iod/Trithiol (1% / 3.7% / 3%, w/w/w) in laminate upon LED@405 nm (100 mW/cm^2). Thickness = 12 µm.



Figure S4. Decay traces of TiQ triplet state (³TiQ) at 440 nm after a laser pulse ($\lambda_{ex} = 385$ nm) of argon (1) and O₂ (2) – satured toluene solution of TiQ.



Figure S5. Cyclic voltammetry of TiQ in $[^{n}Bu_{4}N][PF_{6}]/THF$ (0.2 M electrolyte, room temperature, under N₂).



Figure S6. HAADF-STEM images of Ti NPs inside coatings from A) TiQ/Iod/EPOX system upon a LED@385 nm exposure (44 mW/cm²) under air and B) EPOX/TMPTA blend (50%/50%, w/w) in the presence of TiQ/Iod/Trithiol upon a LED@405 nm exposure (100 mW/cm²) under air. Irradiation time = 800s.