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NANOSTRUCTURED POLYMERS ENABLING STABLE LOW-INTENSITY LIGHT UPCONVERSION

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Photon upconversion is a process in which the energy of two or more photons are combined to produce photons of higher energy. This process can be achieved by various ways, but sensitized triplet-triplet annihilation upconversion (sTTA-UC) was demonstrated to be the method of choice to convert low-power, incoherent light. The upconverted luminescence in sTTA-UC is usually achieved through populating the triplet state of an emitter dye by transferring energy (ET) from a low-energy radiation absorbing moiety that serves as a sensitizer. Then, annihilation (TTA) upon the encounter of two triplet emitter excitons results in the formation of a high-energy fluorescent singlet state that decays by emitting a photon. While this process readily occurs in a degassed solution of matched dyes, where molecular mobility is favored, particular architectures are needed to facilitate efficient ET and TTA in a solid-state material. Furthermore, the sTTA-UC dye pair requires protection from the environment to operate efficiently, as the excited intermediates created upon irradiation are readily quenched by oxygen. Recently, nanostructured glassy polymers were shown to provide protection from air to the sTTA-UC dye pair while simultaneously segregating them in a nanometric liquid environment ensuring efficient diffusion-based ET and TTA. However, the materials suffered from chemical and structural instabilities, reducing the applicability of the concept. In this thesis, the main sources of instability are identified and methods to eliminate them are proposed and investigated. In addition, peculiar characteristics arising from these methods conferring new, enhanced properties to the nanostructured upconverting polymers are investigated. The new generation of this class of materials are made with an adapted polymerization procedure which is based on a new initiation system that produces a tightly confined arrangement of the dyes in the bulk polymer where ET and TTA occur through exciton propagation with a negligible contribution from molecular diffusion. The resulting upconverters possess a significantly improved efficiency and a remarkable stability.

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