Indane-1,3-dione-based push-pull dyes as low fluorescent and highly efficient photoinitiators for free radical polymerization

Michalis Stavrou[1*], Dimitra Ladika[1], Gordon Zyla[1], Frederic Dumur[2], Maria Farsari[1], David Gray[1]

[1]*Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas, 70013 Heraklion, Greece*

[2]*UMR 7273, Aix Marseille Univ., CNRS, ICR, 13397 Marseille, France*

*Corresponding author email: m.stavrou@iesl.forth.gr

Over the past two decades, Multi-Photon Lithography (MPL) has emerged as a highly effective manufacturing technique for crafting complicated three-dimensional (3D) microstructures with sub-microns resolved features.[1] MPL has played a pivotal role in advancing a diverse range of fields including micro-electronics,[2] micro-optics/photonics,[3] biomedicine,[4] microfluidics,[5] and plasmonic devices,[6] among others. In a typical MPL process, a photosensitive material, composed of reactive oligomers and a photoinitiator (PI), is exposed to high-intensity radiation by a tightly focused fs laser pulsed beam. Due to the high laser intensities, the nonlinear optical process of multi-photon absorption is manifested. Consequently, the PI absorbs simultaneously two or more photons through virtual intermediate states, leading to its decomposition into radicals. These radicals induce a cross-linking reaction of the oligomers. Unlike single-photon absorption, multi-photon processes enable the localization of photochemically induced polymerization to the focal point of incident laser beam, resulting in the precise printing of structures with feature sizes below the diffraction limit of light.

The effectiveness of the PI is widely recognized to significantly influence various critical aspects of the printing process, such as the resolution and fabrication time of the 3D microstructures. So far, different synthetic approaches have been proposed to tune the efficiency of PIs, which is generally expressed by their two-photon absorption cross section σ. These approaches involve manipulating different structural parameters of PIs, as for instance, the size, the planarity, the aromatic properties of the monomeric units (e.g., through selective doping of the carbon framework with heteroatoms) and the kind of the peripheral functionalization (e.g., by incorporating electron donating and/or accepting substituents). From the aforementioned strategies, the most successful motif for molecules orientated towards MPL consists of electron donating and accepting functionalities, bridged by a π-conjugated spacer. In that view, significant efforts have been dedicated to synthesize compounds acting as strong electron donors/acceptors to enhance the performance of MPL. The present work assesses the efficiency of newly synthesized indane-1,3-dione-based push-pull dyes as PIs, comparing the findings with previously studied triphenylamine-based aldehydes and standard PIs for MPL applications. The present PIs exhibit strong nonlinear optical properties (i.e., two-photon absorption cross section and second-order hyperpolarizability) resulting in 3D structures with low fabrication threshold and high resolution. Most importantly, the fabricated structures display low fluorescence quantum yield. These findings render them highly promise for advancing applications in photonics, optoelectronics, medicine, and other innovative fields.

References: [1] M. Farsari, B.N. Chichkov; [2] X. Zhou, Y. Hou, J. Lin; [3] H. Wang, W. Zhang, D. Ladika, H. Yu, D. Gailevičius, et al.; [4] R. Luttge; [5] M. Li, W. H. Li, J. Zhang, G. Alici, W. Wen; [6] J.A. Kim, D.J. Wales, A.J. Thompson, G. Yang.