MOLECULAR DESIGN TOWARDS NOVEL PHOTO-INITIATORS WITH INCREASED TWO-PHOTON ABSORPTION CROSS SECTION

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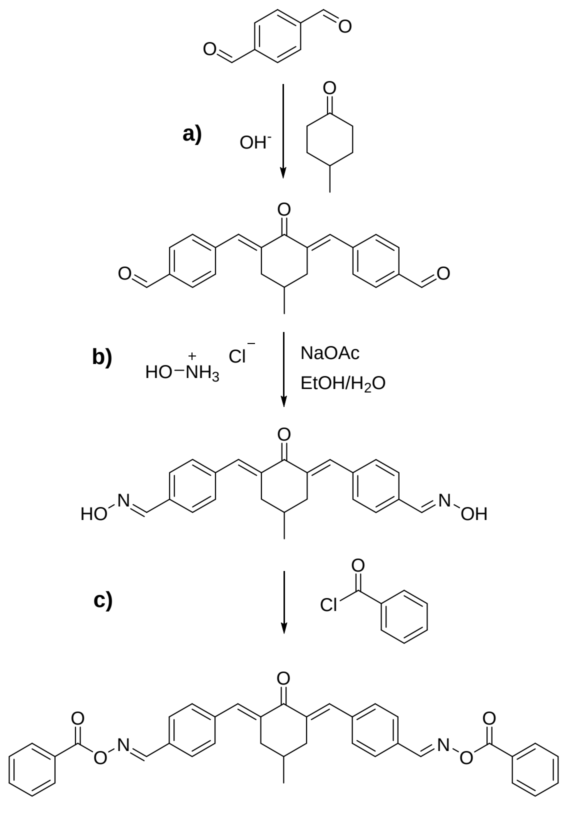
INTRODUCTION

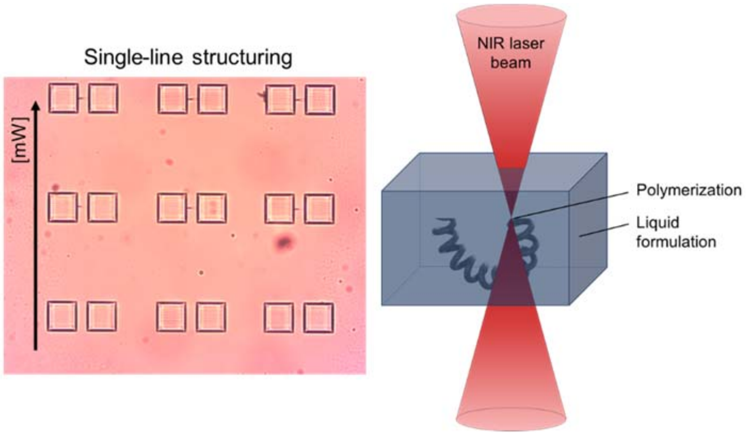
Photopolymerization has become a valuable technique within additive manufacturing technologies (AMTs) to locally crosslink photosensitive polymers with high temporal and spatial control.[1] In order to initiate radical photopolymerization a variety of photo-initiators (PIs) are available. Two-photon polymerization (2PP) has been recently employed within the biomedical sector, since photopolymers can be crosslinked under relatively mild conditions.[2] Two-photon absorption (2PA) is a non-linear optical process, only occurring at the focal point of laser beams, where intensities are high enough for two-photon initiators (2PIs) to absorb the energy of two photons simultaneously. In contrast to one-photon absorption, where molecules are excited to an electronic state, which corresponds to the energy of one photon, 2PA is a process with rather low probability and requires extremely high laser peak powers. Due to the high transparency of biological tissues towards the pulsed infrared laser it is possible to scan the laser through a liquid formulation, enabling 3D printing in the presence of living tissue. For this process, molecules with large 2PA cross sections are needed, to ensure efficient radical polymerization. Planar and multi-polar molecules with electron donating and –withdrawing groups, as well as large delocalized π-electron systems have been known to show large 2PA cross sections. These structural properties of 2PIs have been studied to enhance polarization of molecules and their absorption properties, necessary for 2PP.[3] Continuous development of 2PIs is crucial to ensure efficient photopolymerization of new systems. There are several concepts in order to increase 2PI efficiency, such as reducing the chance of unwanted processes like back electron-transfer (BET). BET simply reverses reaction kinetics of the initiation reaction, thus decreasing 2PI activity. By the introduction of efficiently and irreversibly cleavable functional groups, such as oxime ester functionalities, BET can be minimized.[4]



Picture 1: Synthesis of new two-photon initiators

EXPERIMENTS

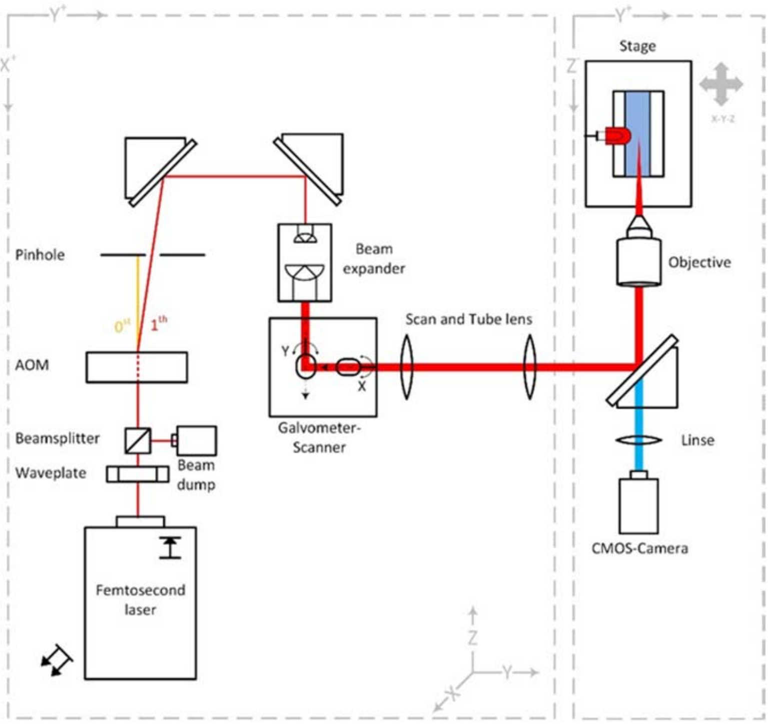
Based on this concept, new cyclic ketone-based 2PIs have been synthesized according to a 3-step synthesis plan (Picture 1). Irreversibly cleavable oxime ester functionalities have been introduced within the molecular structure by selective Claisen-Schmidt condensation of terephthalaldehyde and methyl cyclohexanone. Subsequent synthesis of aldoximes and esterification reaction with acid chlorides led to newly developed 2PIs containing oxime ester moieties. Single-line structuring tests of an acrylic resin containing 2PIs have been performed to evaluate laser power thresholds during 2PP processing (Picture 2). Furthermore, 2PA properties at varying wavelengths have been measured by a fully automatized Z-scan set-up. The experimental set-up for 2PP is depicted in Picture 3.



Picture 2: Single line structuring array of an acrylate resin to determine polymerization threshold of the formulation

RESULTS AND DISCUSSION

Accordingly, a novel 3-step synthetic approach was developed in order to design novel 2PIs. Centrosymmetric conjugated two-photon active chromophores have been developed and characterized accordingly. Single-line structuring tests have been conducted to investigate polymerization thresholds of new formulations. Selective coupling of irreversibly cleavable functional groups (oxime esters) to two-photon active sensitizers led to novel 2PIs with minimized BET.



Picture 3: 2PP set-up for the micro-fabrication of newly developed 2PIs

CONCLUSION

Molecular design towards 2PIs with increased 2PA cross sections is crucial to improve 2PP processing. Constant demand towards improved 2PI efficiency reinforces molecular development of new systems. In order to determine biocompatibility, water-soluble molecules will be synthesized and investigated accordingly. Future experiments will include cell-culture studies to investigate long-term viability of living cells in combination with novel 2PIs.

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