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Cap-Linker-Cap Systems as Efficient Initiators for Two-Photon Polymerization

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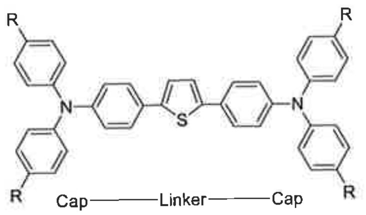
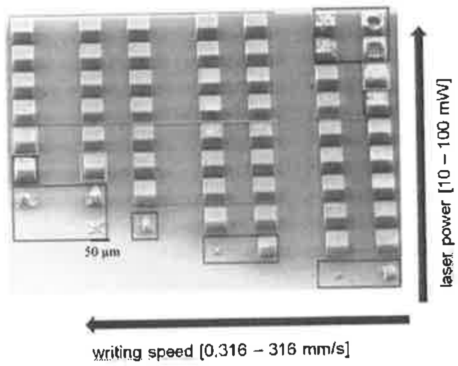
In recent years, two-photon absorption (2PA) has attracted much attention due to its potential applications in materials science and biological imaging, including optical limiting, two-photon fluorescence imaging, photodynamic therapy, three-dimensional (3D) optical data storage, and 3D micro- and nanofabrication via two-photon polymerization and multi-photon processing in general [1-3]. The two-photon polymerization technique would strongly profit from the availability of initiators with large 2PA cross-sections. Therefore, there is a need for engineered organic molecules constituting highly efficient two-photon absorbing initiators (2PIs).

Preliminary results revealed promising properties of a cap-linker-cap type systems [4] **BRA_1T** (Figure 1, a) (linker = thiophene, cap = triphenylamine, R= $-CH_3$) as an efficient 2PI (Figure 1, b). Based on these findings our current research focuses on the alteration of the substituent R in **BRA_1T**, which strongly influences physicochemical properties of the resulting material, like absorption characteristics, ideal processing parameters regarding writing speed and laser power, as well as solubility in the respective monomer formulation. The variation of the substituent R in **BRA_1T** includes electron withdrawing groups such as -F, -CN, $-SO_2Me$ and $-NO_2$ as well as electron donating groups such as $-CH_3$, $-OCH_3$, -^{t}Bu and -TMS.



BRA_1T

(a)



(b)

Figure 1 (a) cap-linker-cap-system BRA_1T. (b) speed-power-screening to determine ideal processing window; colour classification system: green category: excellent structures with straight lines and single lines recognisable; yellow category: good structures with wavy lines or slightly contorted structures; red category: well identifiable structures with errors like holes; blue category: structures are not identifiable as lattices.

The synthetic approach towards these target molecules, their characterization and evaluation of nonlinear absorption properties with Z-scan measurements will be the subject of this contribution. Furthermore, our first results of 3D microstructuring using these compounds as 2PI's will be presented.

[1] M. Rumi, S. Barlow, J. Wang, J. W. Perry, S. R. Marder, Adv. Polym. Sci., 213, 1-95, (2008).
[2] A. Ovsianikov, V. Mironov, J. Stampf, and R. Liska, Expert Rev. Med. Devices 9(6), 613–633 (2012).
[3] J. Shao, Z. Guan, Y. Yan, C. Jiao, Q.-H. Xu, C. Chi, J. Org. Chem., 76, 780–790, (2011).
[4] T. Noda, I. Imae, N. Noma, Y. Shirota, Adv. Mater., 9 (3), 239 – 241, (1997).

High-resolution 3D patterning via multi-photon grafting with aromatic azides

Maximilian Tromayer[1], Zhiquan Li[2], Evaldas Stankevicius[3], Peter Gruber[1], Aliasghar Ajami[4], Wolfgang Husinsky[4], Gediminas Račiukaitis[3], Jürgen Stampfl[1], Robert Liska[2], Aleksandr Ovsianikov[1]

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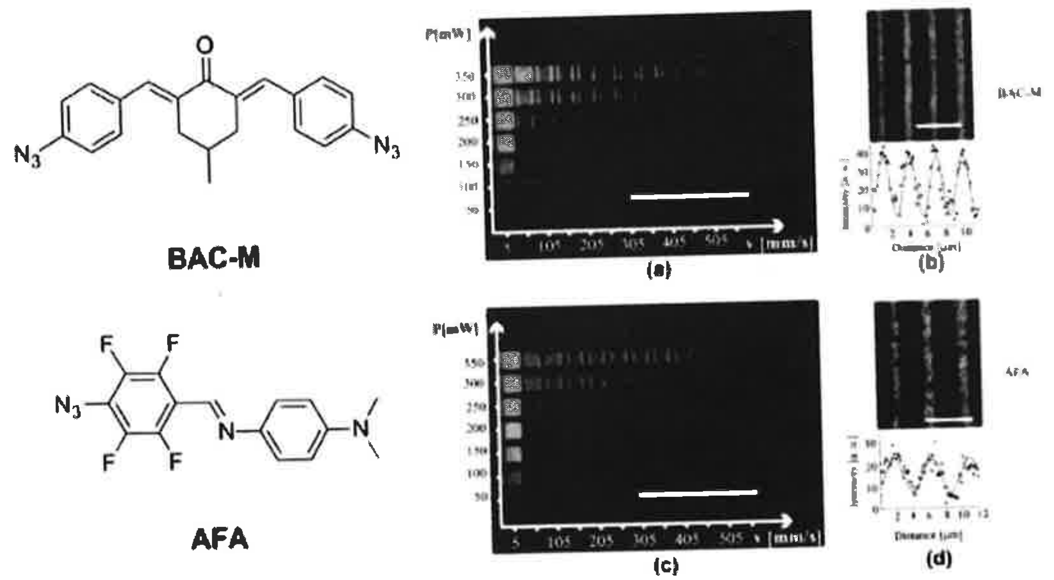
The method of photografting allows the modification of polymer surfaces and matrices by covalent binding of functional molecules in a light activated reaction. It has been widely employed to tailor the physical and chemical properties of polymers such as wettability, adhesiveness, biocompatibility, antifouling, etc. Induction of the grafting process via multi-photon absorption offers the additional benefit of precise spatial and temporal control. The nature of the multi-photon absorption process allows the confinement of induced reactions to a small volume in the focal spot of a femtosecond-pulsed laser and thus grafting of 3D patterns with high resolution.



Structures of the investigated aromatic azides and according patterns obtained via multi-photon grafting

A novel fluoroaryl azide compound (AFA) for photografting was synthesized and compared with the commercially available azide BAC-M. By open aperture z-scan technique it was determined that at the used laser wavelength of around 800nm AFA is a two-photon absorber whereas BAC-M exhibits three-photon absorption. Both azides used for 3D photografting of a PEG-based matrix. Z-scan measurements as well as 3D photografting tests indicated a stronger nonlinear absorption and lower required threshold intensity for photografting in case of AFA compared to BAC-M. As a result AFA exhibits a broader processing window. On the other hand, due to the lower probability of the three-photon absorption in case of BAC-M, it allows writing of finer lines and thus patterns with features of higher resolution. The choice of the appropriate compound for 3D grafting will depend on the final application and the requirements associated with the resolution and post-modification protocol.

(1) Ovsianikov, A., Li, Z., Torgersen, J., Stampfl, J., and Liska, R., *3D Photografting: Selective Functionalization of 3D Matrices Via Multiphoton Grafting and Subsequent Click Chemistry*, Adv. Funct. Mater. 2012. **22**(16): p. 3527–3527.

(2) Li, Z., Ajami, A., Stankevičius, E., Husinsky, W., Račiukaitis, G., Stampfl, J., Liska, R. and Ovsianikov, A., *3D photografting with aromatic azides: A comparison between three-photon and two-photon case.* Optical Materials, 2013. **35**(10): p. 1846-1851.

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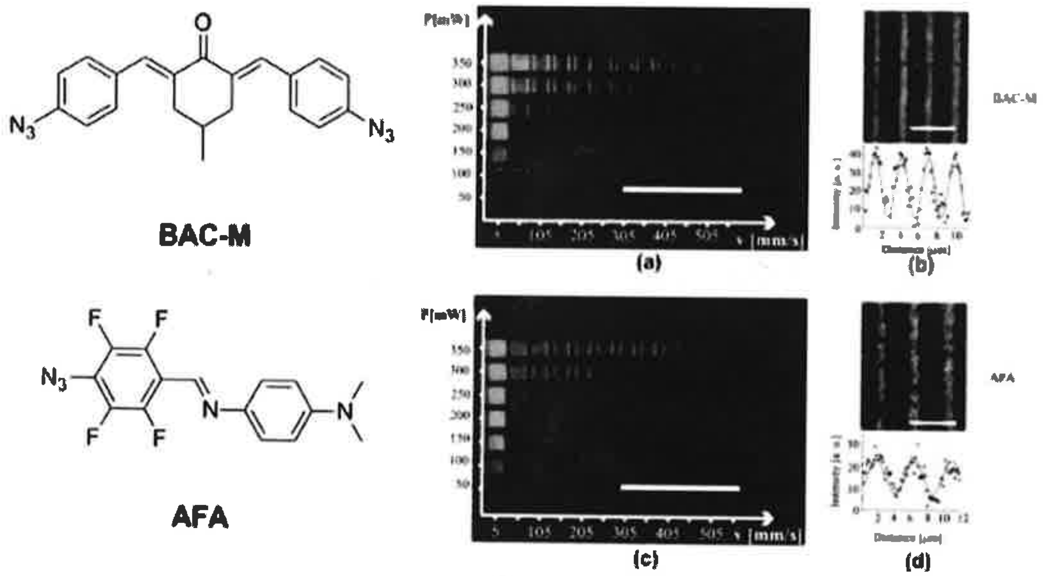

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Laser Photofabrication of Cell-Containing Hydrogel Constructs

Peter Gruber[1], Marica Markovic[1], Katrin Hölzl[1], Maximilian Tromayer[2], Sandra Van Vlierberghe[3], Peter Dubruel[3], Robert Liska[2], Jürgen Stampfl[1] and Aleksandr Ovsianikov[1]

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Two-photon polymerization (2PP) is based on localized cross-linking of photopolymers, induced by two-photon absorption of femtosecond laser pulses [1]. Compared to other additive manufacturing technologies, 2PP offers higher spatial resolution and a possibility to produce 3D structures within the volume of the sample, without the necessity to deposit the material layer-by-layer. In the recent years 2PP attracted much attention as a tool for the fabrication of tissue engineering scaffolds. Incorporating living cells in the fabrication process is advantages with regard to initial cell density and distribution in the scaffold. Light-induced cell encapsulation can be executed at mild pH and temperature conditions. Furthermore it provides advantages of temporal and spatial control of the polymerization process. Cells and tissue are transparent in the near-IR wavelength range commonly used for 2PP, besides the employed laser radiation parameters are known to be harmless to cells. In order to incorporate living cells during 2PP, suitable materials supporting the viability of cells throughout the fabrication process have to be developed.

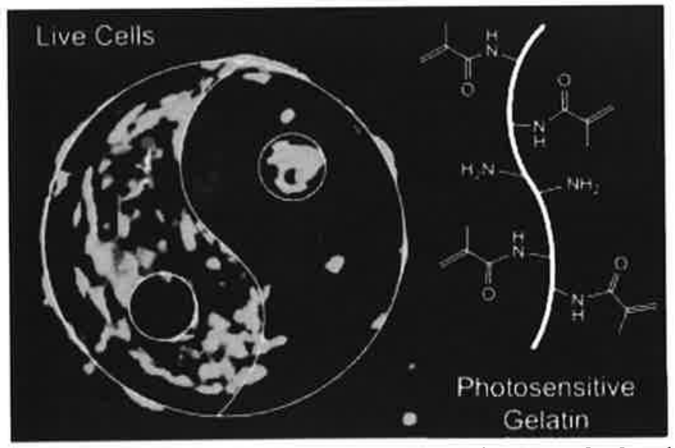

Figure 1 (left) Proliferation of MG63 cells trapped within the voids of a 2PP hydrogel structure after 3 weeks in culture. (right) Chemical structure of methacrylamide-modified gelatin (gelMOD)

In this contribution our first results on 2PP fabrication of cell-containing hydrogel constructs are presented. Gelatine-based material formulations with up to 80% cell culture medium have been processed successfully. The cells trapped within the 2PP-produced structures stayed viable and continued to proliferate. The live/dead staining after 3 weeks revealed viable cells occupying most of the space within the 3D hydrogel constructs [2]. The presented results indicate the general practicability of 2PP for 3D processing of cell-containing materials. Potential applications of this highly versatile approach span from precise engineering of 3D tissue models to the fabrication of cellular microarrays.

[1] A. Ovsianikov, V. Mironov, J. Stampf, and R. Liska, Engineering 3D cell-culture matrices: multiphoton processing technologies for biological and tissue engineering applications, Expert Rev. Med. Devices 9(6), 613–633 (2012).
[2] A. Ovsianikov, S. Mühleder, J. Torgersen, Z. Li, X.-H. Qin, S. Van Vlierberghe, P. Dubruel, W. Holnthoner, H. Redl, R. Liska, and J. Stampfl, Laser Photofabrication of Cell-Containing Hydrogel Constructs, Langmuir, 131010115717001 (2013).

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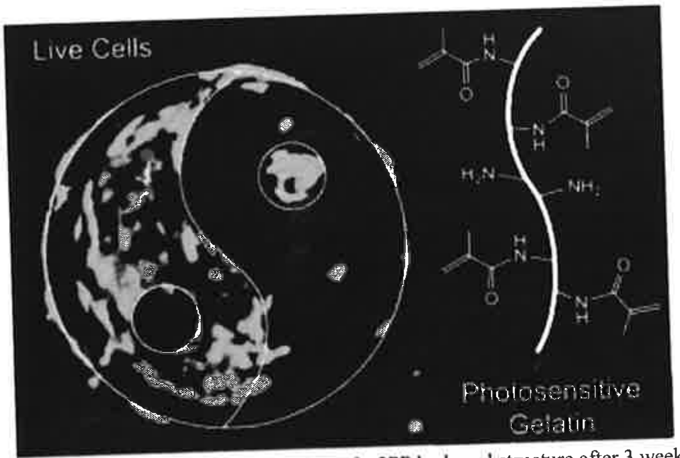

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