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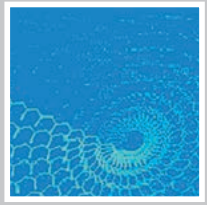

Polymer and Colloid Highlights

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When Photoswitches Meet 3D-Printing

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Donor–acceptor Stenhouse adducts (DASAs)[1] are a new class of T-type organic photoswitches first reported in 2014 that change between an apolar colored state to a highly polar colorless isomer (Fig. 1A). DASAs exhibit a range of promising properties such as negative photochromism, visible light activation and modular synthesis. DASA-materials have been proposed for visible light-controlled drug delivery, colorimetric sensors, fluorescent modulation of dyes, and photoinduced deadhesion of polymers from glass surfaces, among other applications. We and others have developed DASA-polymer conjugates and investigated their properties and applications.[2] Despite much progress, the fabrication of DASA-based photochromic materials has been limited to conventional methods such as mold casting and spin coating.

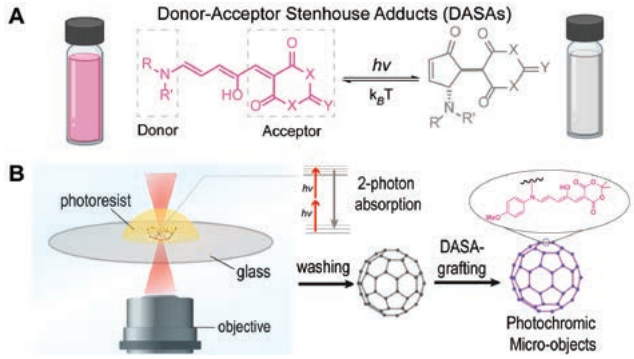

Fig. 1. **(A)** General structures for DASAs and their photoswitching between the open triene (colored) and the closed cyclopentenone (colorless) isomers. R/R': alkyl or aryl; X: O or N. **(B)** Two-photon 3D microprinting of DASA-containing photochromic micro-objects.

Advances in light-based 3D-printing techniques have enabled controlled fabrication of complex polymeric microstructures. One promising high-resolution 3D-printing technique is two-photon polymerization (2PP), which exploits non-linear absorption and allows direct laser writing of arbitrary structures with submicron-scale accuracy.[3] However, an efficient photoresist for custom 3D fabrication of photochromic micro-objects is still lacking.

To tackle these issues, we developed a modular thiol-ene resin for custom fabrication of polymer networks with covalently bounded DASA photoswitches by 2PP (Fig. 1B).[4] An ene-terminated precursor was synthesized for co-polymerization with multifunctional thiol- and ene-terminated monomers. After sub-stoichiometric two-photon-induced thiol-ene crosslinking, DASAs were formed by exposing the networks to furan adducts. This approach circumvents photodamage to the dye by separating the functionalization from the crosslinking reaction; moreover, it allowed us to create a library of DASA-containing polymer networks from a single starting amine-modified polymer. These highly efficient thiol-ene resins enabled fine-tuning the physical properties such as mechanics and glass transition temperature (T_g) of the networks by changing the stoichiometric ratio between thiol and ene groups. The variation of matrix mechanics and T_g influences the photoswitching kinetics of DASAs. For instance, increasing the crosslinking degree decreases the recovery kinetics. The chemical structure of covalently bound DASA moieties (*i.e.* the type of donor/acceptor) had a strong effect on their photoswitching kinetics, similarly to what has been found for DASAs in solution.

Based on these findings, the thiol-ene resins were exploited for custom two-photon microfabrication using a commercial Nanoscribe 3D microprinter. By tuning the processing parameters (laser power, writing speed, and line number), the materials are processable in a wide processing window. The highly efficient thiol-ene photo-click reactions enabled direct laser writing at high writing speeds up to 50 mm/s. Complex C_{60}-shaped microstructures were fabricated with excellent structural fidelity. After functionalization with furan adducts, the photoswitching of DASA-containing microstructures was analyzed by monitoring the fluorescence recovery of DASAs after photobleaching by time-lapse confocal microscopic imaging.

To the best our knowledge, this is the first study that demonstrates 3D-printing of photochromic micro-objects by high-resolution two-photon photolithography and subsequent modular functionalization with visible light-responsive photoswitches. In the future, we envisage that the presented methodology may enable new applications whereby digitally fabricated photochromic micro-objects serve as smart multi-addressable switches and optical filters, and photoswitching is realized with high degree of control in a spatially and temporally controlled fashion.

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