A Novel Two-Photon Absorbing PAG and Its Application in 3-D Microfabrication

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This paper reports on a novel photoacid generator (PAG) used as an initiator, in a negative resist, for 3-D microfabrication. The PAG was designed to have a high two-photon cross section and to trigger the crosslinking of epoxy monomers or resins by two photon (2PA) induced, acid catalyzed, ring opening polymerization. This initiator, 9, 9-diethyl-[bis-(styryltriphenyl sulfonium hexafluoro phosphonate)] fluorene (DAS-2), was prepared by means of a four-step synthesis starting from flourene. The negative photoresist was composed of DAS-2 and Epon SU-8. One-photon polymerization was achieved by the projection of a photomask on the resists using high intensity broadband UV radiation. Two-photon microfabrication was performed by inducing the photolysis of DAS-2 upon high intensity femtosecond 760 nm laser irradiation.

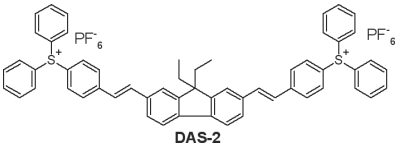
Introduction

In 1972, the polymer industry had the pressing need to replace the thermally cured, solvent-based, UV-curing procedures that had traditionally been employed. This spawned the development of aryl sulfonium and aryl iodonium salts as PAGs, molecules that form Brønsted acids upon photoexcitation, to induce the photopolymerization of epoxides, vinyl ethers, and the crosslinking of epoxy polymer resins.[1, 2] Since their discovery, the use of PAGs has been widely adopted by the polymer industry in coatings, paints, anti-corrosives and electronics.[3] The use of PAGs in epoxide photoresists has been extensively studied for 2-D and 3-D lithographic patterning induced by one-photon absorption (1PA) and two-photon absorption (2PA).[4, 5]

In recent years, the use of two-photon absorption (2PA) has been increasingly employed in various scientific and technological fields. Many of these applications rely on the 2PA probability being directly proportional to the square of the incident light intensity ($dw/dt \propto I^2$) (while one-photon absorption (1PA) bears a linear relation to the incident light intensity, $dw/dt \propto I$).[6] This intrinsic property of 2PA has enabled the confinement of photochemical processes to increasingly smaller spatial resolution, which has been exploited in many different fields such as optical data storage,[7-9] fluorescence microscopy,[10, 11] and 3-D microfabrication.[12,13] Recently, very versatile two photon, 2-D patterning techniques have been reported, in which projection of any given object is used as a photomask to obtain lateral

features sizes as small as 120 nm.[14] There have been studies of successful two photon microfabrication using commercial PAGs;[13,15] however, the two-photon absorption cross section of these initiators has been reported to be low.[16] In 2003, the synthesis of a PAG for two-photon 3-D microfabrication was developed and its potential use in the fabrication of MEMs was evaluated.[17,18]

This paper reports on a novel PAG used as a photoinitiator, in a negative resist, for 3-D microfabrication. The PAG was designed to have a high, two-photon absorption cross-section and to trigger the crosslinking of epoxy monomers or resins by 2PA-induced, acid catalyzed, ring opening polymerization. It has been observed that symmetrical conjugated systems with two electron-donating groups (D) or electron accepting subtituents (A) tend to have significant 2PA properties, and high 2PA absorption cross sections.[19,20] Based on the high thermal and photophysical stabilities of the florenyl π-system,[21] fluorene was chosen as the core structure when designing the PAG. Because fluorene can be readily substituted in its -2, -7, and -9 positions a stilbene motif was introduced (-2, -7 positions) in order to extend the π-conjugation, and ultimately two acceptor groups (triaryl-sulfonium salts) were introduced as sulfonium derivatives to obtain DAS-2



DAS-2

Experimental Section

Materials

Shell Epon SU-8 (formaldehyde, polymer with (chloromethyl) oxirane and 4,4'-(1 methylethylidene)bis[phenol]) and Sartomer K-126 (3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexane carboxylate) were used as received. The synthesis and characterization of DAS-2 (1) will be described elsewhere. All solvents were used as received. The glass resolution targets were purchased from Edmund Scientific (negative slide with the 1951 USAF test pattern).

Instrumentation

One-photon (conventional) polymerization of the resist was carried out by exposing the Epon SU-8 resin with a Loctite 97034 light source equipped with a 200 W mercury lamp as a radiation source and an internal shutter that was used to control the exposure times (one-photon polymerization experiments). The photomask was either projected or simply placed on the dry resist system (as a contact mask). The waveguide of the Loctite was focused into the condenser of an Olympus IX-81 confocal microscope. The DIC (differential unterference contrast) and fluorescence images of the structures produced by one-photon excitation were recorded on an Olympus IX-81 confocal microscopy system equipped with a Hamamatsu EM-CCD C9100 digital camera.

Thin films were spin-coated onto No. 1 glass microscope cover slips or 2.5 x 2.5 cm microscope glass slides (Fisher) with a spin-coater from Headway Research Inc. The film thickness of polymer films is calculated by focusing the glass surface and the polymers upper surface and determining how much the z stage of the microscope had moved and confirmed by a micrometer. Two-photon polymerization, DIC, and fluorescence images of polymer films were performed on a modified Olympus Fluoview laser scanning confocal microscopy system equipped with a broadband, tunable Coherent Mira Ti:Sapphire laser (tuned to 760 nm, 115 fs pulse width, 76 MHz repetition rate), pumped by a 10 W Coherent Verdi frequency—doubled Nd:YAG laser, and a two channel detection system (two Hamamatsu photomultiplier tubes with band-pass filters, channel 1: 510-550 nm, channel 2: 585-610 nm). In two-photon polymerization experiments, the exposure time was controlled by means of an electronic shutter and an electronic stage both from Thor Labs.

The DAS-2 PAG, 9,9-diethyl-[bis-(styryltriphenyl sulfonium hexafluoro phosphonate)]fluorene, was made by means of a four-step synthesis starting from flourene. The synthetic procedure for the synthesis of DAS-2 will be published elsewhere. The negative photoresist was composed of DAS-2 (1) and Epon SU-8. One-photon microfabrication was achieved by the projection of a photomask on the resists using high-intensity broadband UV radiation. Two-photon polymerization was performed by inducing the photolysis of DAS-2 (1) upon high intensity femtosecond 760 nm laser irradiation.

General Procedures

Glass Functionalization

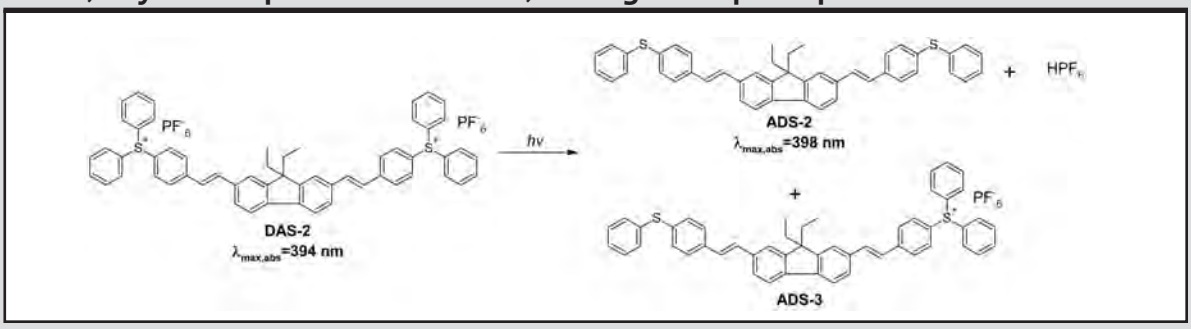
No. 1 glass microscope cover slips or 2.5 x 2.5 cm microscope glass slides were treated with a piranha solution (7:3; sulfuric acid: 30% hydrogen peroxide) for 10 min at 60 °C and dried under a stream of nitrogen. The etched slides were placed in a 30% solution of 3-aminotrimetoxy silane in ethanol and dried again with nitrogen.

Spin Coating

Epon SU-8 and Sartomer K-126 (in an 8:2 ratio) were mixed with 1% weight of DAS-2 and a minimal amount of propylene carbonate. The homogeneous mixture was dissolved (30%) in toluene. The resulting mixture was filtered through a 0.45 µm glass filter. Once filtered the resin was spin coated on the substrates (1. 500 rpm, 10 seconds and 2. 1,000 rpm, 30 seconds).

FIGURE 1

Photolysis of DAS-2 when exposed to UV-A/UV-B radiation will primarily generate hexaflouro-phosphoric acid, to induce crosslinking, and the highly fluorescent ADS-2, a synthetic precursor of DAS-2, among other photoproducts



The samples were dried in a vacuum oven over night at 80ºC.

Exposure and Developing

The resin was exposed to the broadband UV radiation through (one-photon) and 760 nm (two-photon) for a number of different exposure times. Post-exposure baking was carried out on a hotplate at 90ºC (10 min). The resist was developed by carefully washing away the unexposed resist with acetone, followed by isopropanol. The slide was then dried under nitrogen.

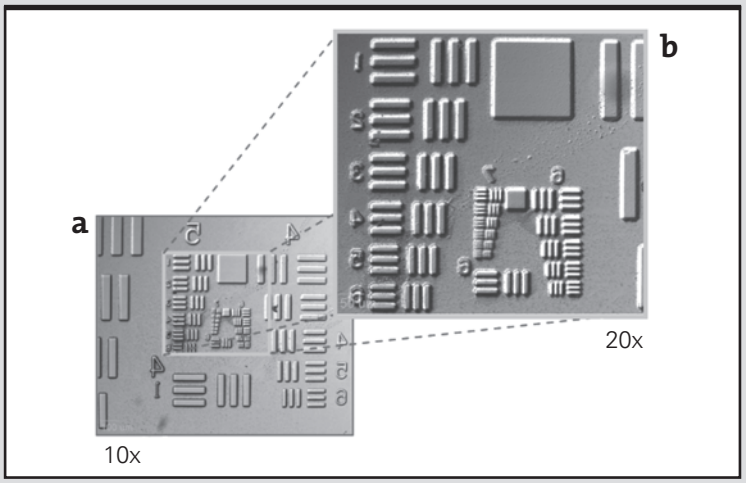
Results and Discussion

The resist was deposited onto a glass cover slip by means of spincoating as indicated above, and left to dry overnight (see details in the experimental section above, also see Figure 4). In the one photon fabrication experiments, the resist system, composed of Epon SU-8 and Sartomer K-126 (in an 8:2 ratio) as epoxy monomers and DAS-2 as the photoacid generator, was exposed to UV-visible radiation of a high-pressure mercury lamp focused through a liquid waveguide into the stage of the confocal microcope. The microscope stage helped to further focus the light through the photomask (USAF resolution mask) onto the surface of the resist. Once exposed, the resist was developed and the same microscope was used to record the DIC and fluorescent images. In the DIC images of the structure resulting from the contact photomask experiments (Figures 2a and 2b) clear, undistorted structures were obtained with up to ~3.5 µm size features.

The photodecomposition of triaryl sulfonium has been known to generate Brønsted acids. Typically the counter ion of these salts is a heavy atom halide salt (commonly AsF_6^-, SbF_6^-, PF_6^-, BF_4^-). In these cases, the acid generated from this photolysis is a superacid. The superacid anions are very bulky and quite poor nucleophiles, which is why they are such efficient photoinitiators for acid-catalyzed ring opening polymerizations of epoxy-resins. Among the many

FIGURE 2

DIC images of microstructure generated by one-photon contact lithography using USAF target resolution masks



Exposure time: 300 seconds
a) Objective 10x (NA=.30); 62 ms.
b) Objective 20x (NA=.45); 250 ms.

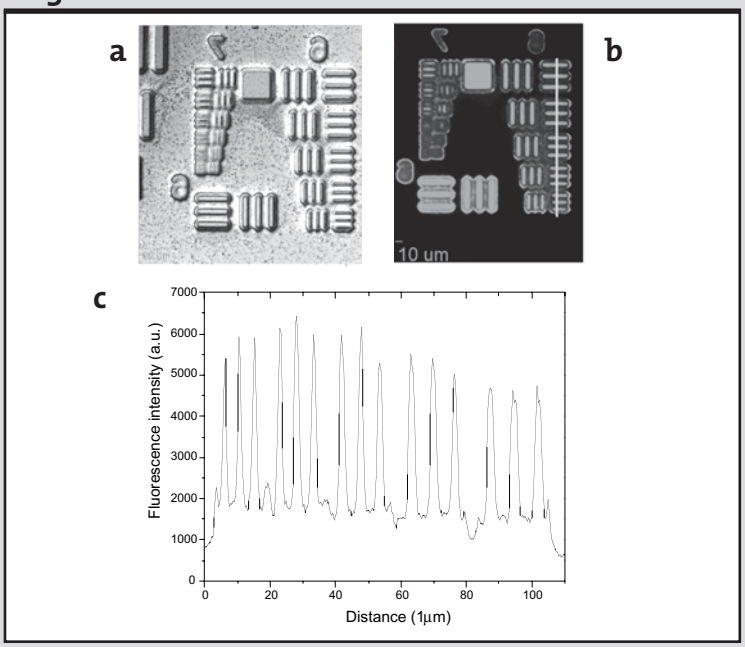
products of decomposition of the aryl sulfonium salts, the most abundant is the diaryl sulfide (Figure 1). Because DAS-2 has two sulfonium functionalities, it will probably have the symmetric and unsymmetrical aryl sulfide products. The symmetrical aryl disulfide (ADS-2, Figure 1) is the synthetic precursor of DAS-2, and was necessarily characterized during the synthesis of the sulfonium salt. ADS-2 was found to possess a fluorescence quantum yield of 0.98. When polymerization is carried out, this diarylsulfide (ADS-2) and monosulfide (Figure 1) among other photolysis products are entrapped in the polymer matrix. The high fluorescence quantum yield of ADS-2 (0.98) then allows one to observe highly fluorescent structures after development (Figure 4). Such a property also enables one to see cracks and defects in structures that would otherwise be difficult to detect by other means. This property may prove to be useful in applications where small structural defects need to be detected.

The highly fluorescent structures that remain after exposure are shown in Figure 3b. The images of these structures were captured using a filter cube (excitation bandpass filter 377/50; emission bandpass filter 525/40). The fluorescence intensity graphs (Figure 3c) show the high contrast difference between the crosslinked microstructures and void spaces were the non-crosslinked polymer was washed away. This suggests how fluorescence scanning of a structure can be used to detect stress fractures or tiny cracks in a microstructure.

Prior to spin coating, the glass slides were functionalized with 3-aminopropyltriethoxy silane to enhance structure adhesion to the glass substrate upon exposure. Since the absorption DAS-2 possesses a maximum in the absorption spectrum at 394 nm, the profile output from the waveguide of Loctite 97034 was ideal for one photon

FIGURE 3

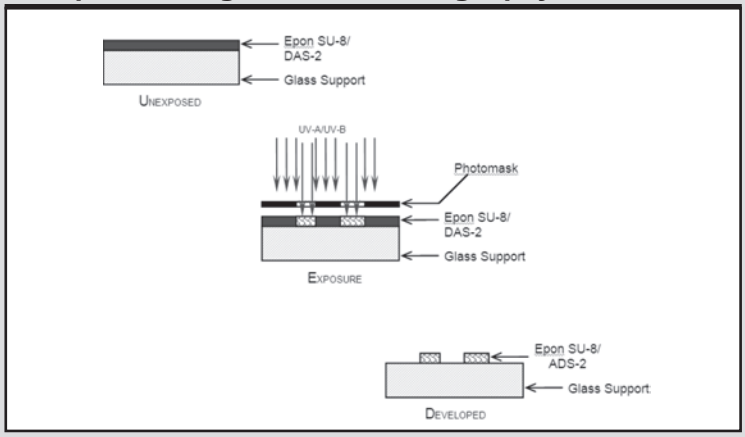
Images of microstructure generated by one-photon contact lithography using USAF target resolution masks



a) DIC (40x objective; NA=0.60; 62 ms).
b) fluorescence (40x objective; NA=0.60; 165 ms). Exposure time: 300 s.
c) fluorescence intensity along the line traced in b).

FIGURE 4

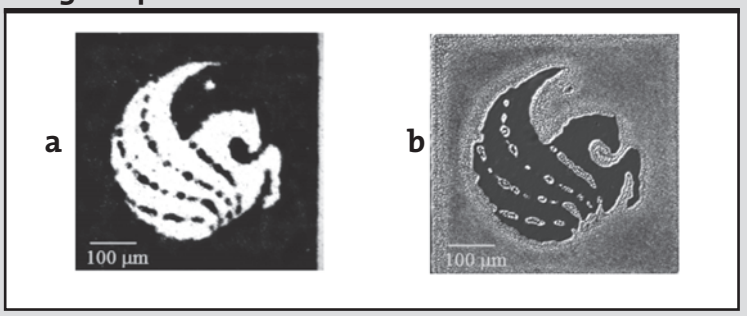
One-photon negative tone lithography



After crosslinking, the highly fluorescent photoproduct ADS-2 is entrapped inside the polymer matrix resulting in highly florescent microstructures.

FIGURE 5

Image of photomask



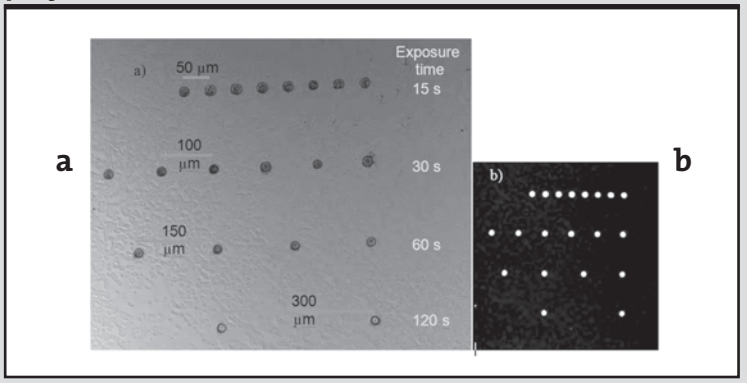
a) DIC image of photomask.
b) DIC image of microstructure resulting after exposure through a projected photomask and development (10x objective, NA=0.30, 130 s exposure time).

curing, as it has sharp maxima at 375 and 405 nm. The optimum exposure time was determined to be 300 seconds. Longer exposure times resulted in loss of resolution, while insufficient exposure leads to poor crosslinked structures that would either swell or wash away from the glass surface during development. The photomasks that were projected (Figure 5b) required less exposure (150 s) than the structures obtained by the contact mask method (Figures 2a,b and 3a,b) because the thickness of the glass of the contact mask reduced the input intensity that ultimately reached the resist.

Preliminary data indicated that the 2PA absorption maximum of DAS-2 was approximately 760 nm; therefore, two-photon induced polymerization was performed at this wavelength. The resist was placed on the stage of the microscope and the laser beam focused into the resist. Because 2PA and hence fluorescence emission is confined to extremely small volumes, precise focusing of the beam was of the essence. The focusing process was, to a large extent, aided by the inherent fluorescence of the PAG (fluorescence quantum yield DAS-2 0.78). Kawata *et al*. have also reported two-photon fluorescence being very helpful when focusing the beam into polymer matrices in two-photon polymerization.[22] In seeking an optimal exposure time the resist was submitted to radiation of the same output intensity (0.858 W) during different time intervals. The exposure time, controlled by an electronic shutter, was steadily increased from 15-120 seconds. In the first line (Figure 6a), eight bits were made, the exposure time was 15 seconds for each bit and the separation between bits 50 µm. In the second line, six bits were made every 100 µm by exposing for 30 seconds; this line was separated from the others by 150 µm. As the exposure time and the distance between the bits increased, the number of bits was decreased, creating an asymmetric pattern that would be easily interpreted after developing.

FIGURE 6

Image produced by two photon-induced polymerization



a) DIC image of bits produced by two-photon induced polymerization (λ: 760 nm; Input: 0.858 W; 40x objective; NA = 0.85).
b) Fluorescence image of microstructure in (a) one-photon (λ: 380 nm) excitation; band-pass emission filter 510-550 nm.

Although two-photon polymerization was achieved (Figure 6a), the bit size didn't correspond to the exposure time. One would expect to see smaller bit sizes at shorter exposure times. However, no significant difference in bit diameter was observed. This was probably because, even at the shortest exposure times, 15 seconds, the resist was overexposed and acid diffusion within the polymer matrix around the exposed area generated an "aureole" or "halo" effect, impeding the system to show its resolution limits. All of the 15 second bits exhibit small cavities, a porosity probably due to the poor crosslinking of the polymer, which translates in swelling during the development stage. This porosity was reduced as the exposure time was

increased because more acid was generated, resulting in a more fully crosslinked resist. Just as was observed for the one photon microstructures, the bits resulting from the two-photon polymerization also exhibited fluorescence as shown in Figure 6b.

Conclusions

DAS-2 is a promising addition to the very few 2PA PAGs that have been reported. Its intrinsic fluorescence is a helpful tool during the experimental intricacies of the two-photon polymerization and the high fluorescence quantum yield of its main photoproduct, ASD-2 (0.98), enables the fabrication of fluorescent microstructures through one- and two-photon induced photolithography. Moreover, preliminary measurements carried out in our lab indicate that ASD-2 has a high 2PA absorption cross section. This important feature gives the fluorescent images of the generated microstructures a much higher resolution, enabling the detection of smaller defects by means of fluorescence imaging. Finally, even though the true two-photon resolution of this system has yet to be fully evaluated, DAS-2 is a promising candidate for two-photon induced cationic ring opening polymerization of epoxides and epoxy resins. ◗

Reference

1. Crivello, J. V.; Lam, J. H. W. Diaryliodonium Salts-New Class of Photoinitiators for Cationic Polymerization, *Macromolecules* 1977, 10, (6), 1307-1315.
2. Crivello, J. V.; Lam, J. H. W. New Preparation of Triarylsulfonium and Triarylselenonium Salts Via Copper(Ii)-Catalyzed Arylation of Sulfides and Selenides with Diaryliodonium Salts, *Journal of Organic Chemistry* 1978, 43, (15), 3055-3058.
3. Crivello, J. V., The discovery and development of onium salt cationic photoinitiators, *Journal of Polymer Science Part A-Polymer Chemistry* 1999, 37, (23), 4241-4254.
4. Jeon, S.; Malyarchuk, V.; Rogers, J. A.; Wiederrecht, G. P. Fabricating three dimensional nanostructures using two photon lithography in a single exposure step, *Optics Express* 2006, 14, (6), 2300-2308.
5. Kim, E. K.; Ekerdt, J. G.; Willson, C. G. Importance of evaporation in the design of materials for step and flash imprint lithography, *Journal of Vacuum Science & Technology B* 2005, 23, (4), 1515-1520.
6. Goeppert-Mayer, M. *Ann. Phys. (Paris)* 1931, 9, 273.
7. Parthenopoulos, D. A.; Rentzepis, P. M., 3-Dimensional Optical Storage Memory, *Science* 1989, 245, (4920), 843-845.
8. Corredor, C. C.; Huang, Z. L.; Belfield, K. D. Two-photon 3-D optical data storage via fluorescence modulation of an efficient fluorene dye by a photochromic diarylethene, *Advanced Materials* 2006, 18, (21), 2910-2914.
9. Belfield, K. D.; Schafer, K. J. A new photosensitive polymeric material for WORM optical data storage using multichannel two-photon fluorescence readout, *Chemistry of Materials* 2002, 14, (9), 3656-3662.
10. Denk, W.; Strickler, J. H.; Webb, W. W. 2-Photon Laser Scanning Fluorescence Microscopy, *Science* 1990, 248, (4951), 73-76.
11. Schafer-Hales, K. J.; Belfield, K. D.; Yao, S.; Frederiksen, P. K.; Hales, J. M.; Kolattukudy, P. E. Fluorene-based fluorescent probes with high two-photon action cross-sections for biological multiphoton imaging applications, *Journal of Biomedical Optics* 2005, 10, (5).
12. Maruo, S.; Nakamura, O.; Kawata, S. Three-dimensional microfabrication with two-photon-absorbed photopolymerization, *Optics Letters* 1997, 22, (2), 132-134.
13. Belfield, K. D.; Schafer, K. J.; Liu, Y. U.; Liu, J.; Ren, X. B.; Van Stryland, E. W. Multiphoton-absorbing organic materials for microfabrication, emerging optical applications and non-destructive three-dimensional imaging, *Journal of Physical Organic Chemistry* 2000, 13, (12), 837-849.
14. Kaehr, B.; Shear, J. B. Mask-directed multiphoton lithography, *Journal of the American Chemical Society* 2007, 129, (7), 1904-+.
15. Belfield, K. D.; Ren, X. B.; Van Stryland, E. W.; Hagan, D. J.; Dubikovsky, V.; Miesak, E. J. Near-IR two-photon photoinitiated polymerization using a fluorone/amine initiating system, *Journal of the American Chemical Society* 2000, 122, (6), 1217-1218.
16. Schafer, K. J.; Hales, J. M.; Balu, M.; Belfield, K. D.; Van Stryland, E. W.; Hagan, D. J. Two-photon absorption cross-sections of common photoinitiators, *Journal of Photochemistry and Photobiology A-Chemistry* 2004, 162, (2-3), 497-502.
17. Yu, T. Y.; Ober, C. K.; Kuebler, S. M.; Zhou, W. H.; Marder, S. R.; Perry, J. W. Chemically amplified positive resists for two-photon three-dimensional microfabrication, *Advanced Materials* 2003, 15, (6), 517-521.
18. Kuebler, S. M.; Braun, K. L.; Zhou, W. H.; Cammack, J. K.; Yu, T. Y.; Ober, C. K.; Marder, S. R.; Perry, J. W. Design and application of high-sensitivity two-photon initiators for three-dimensional micro-fabrication, *Journal of Photochemistry and Photobiology a-Chemistry* 2003, 158, (2-3), 163-170.
19. He, G. S.; Bhawalkar, J. D.; Zhao, C. F.; Park, C. K.; Prasad, P. N. 2-Photon-Pumped Cavity Lasing in a Dye-Solution-Filled Hollow-Fiber System, *Optics Letters* 1995, 20, (23), 2393-2395.
20. Ehrlich, J. E.; Wu, X. L.; Lee, I. Y. S.; Hu, Z. Y.; Rockel, H.; Marder, S. R.; Perry, J. W. Two-photon absorption and broadband optical limiting with bis-donor stilbenes, *Optics Letters* 1997, 22, (24), 1843-1845.
21. Belfield, K. D.; Bondar, M. V.; Przhonska, O. V.; Schafer, K. J. One- and two-photon photostability of 9,9-didecyl-2,7-bis(N,N-diphenylamino)fluorene, *Photochemical & Photobiological Sciences* 2004, 3, (1), 138-141.
22. Sun, H. B.; Tanaka, T.; Takada, K.; Kawata, S. Two-photon photopolymerization and diagnosis of three-dimensional micro-structures containing fluorescent dyes, *Applied Physics Letters* 2001, 79, (10), 1411-1413.

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