تولید میکرو/نانو ساختارهای سه بعدی با استفاده از پالسهای لیزری فمتوثانیه

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چکیده
پالسهای لیزری فمتوثانیه به دلیل کوتاهی طول پالس دارای توان لحظه ای بسیار بالایی می باشند طوری که برهم کنش آنها با هر ماده ای منجر ایجاد تغییرات لحظه اي و یا حتي ماندگار می شود. ما از این پالسها برای تولید ساختارهای سه بعدی پلیمری در ابعاد میکرون و رزولوشن نانومتری استفاده کرده ایم. اساس کار بر پایه جذب دو فوتونی است که امکان تولید ساختارهایی با رزولوشن بهتر از حد پراش را فراهم می کند. در این کار از لیزر فمتوثاینه استفاد شده که طول موج آن در بازه ۷۰۰ تا ۹۰۰ نانومتر کوك پذیر است و پالسهایی ۷۰ فمتوثانیه با تکرار ۸۰ مگاهرتز و انرژیی ۲۵ نانو ژول تولید می کند. رزین که مخلوطی از یک مونومر و یک آغازگر دو فوتونی است با جذب انرژی پالسهای فمتوثانیه ای به پلیمر تبدیل می شود. آغازگرهای دو فوتونی مختلفی برای تولید ساختارهای پلیمری استفاده شدند. ضریب جذب دو فوتوني آغازگرهاي دو فوتوني با تکنيك زي-اسکن اندازه گيري شده و برای هر آغازگر سرعت اسکن و انرژی پالس لیزری بهینه را طوري پيدا کرده ایم تا ساختارهایی با بهترین کیفیت و رزولوشن تولید شود. خطوط پلیمری با ضخامت کمتر از ۱۰۰ نانو متر و ساختارهایی با ابعاد چند ده میکرون قابل تولید با این شیوه می باشد از این رو به این ساختارها به طور دقیق می توان میکرو/نانو ساختار اطلاق کرد.
کلیدواژه‌ها: میکرو/نانو ساختارها ، پلیمریزاسیون دو فوتونی، فوتو پلیمریزاسیون، آغازگر دو فوتونی، لیزر فمتوثانیه، جذب دو فوتونی، اپتیک غیر خطی

3D micro-nano structuring using femtosecond laser pulses

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Abstract
Femtosecond laser pulses have high peak intensity due to their very short duration thus permanent changes can be appeared in materials as a consequence of interaction with femtosecond pulses. We have used femtosecond pulses in order to create polymeric 3D micro-structure with nonomerter resolution. This technique is based on two-photon absorption (2PA) which provides structuring with resolution beyond the diffraction limit. In this work we used a titanium-sapphire (Ti-sapp) laser producing 70 fs, 25 nJ pulses at 80 MHz repetition rate which can be tuned from 700 nm to 900 nm. A mixture of a monomer with a two-photon initiator (2PI), called resin, turns to polymer after absorbing femtosecond laser pulses. In this process the laser beam is focused inside the resin using a high numerical objective. Different 2PIs were examined for 2PP. The 2PA cross section of examined 2PIs was measured using Z-scan technique. For each 2PI the pulse energy and scanning speed were optimized in order to achieve the best quality and highest resolution. Using this unique technique it is feasible to create micro scale 3D structures with resolution better than 100 nm thus our products can be indeed considered as micro/nano structures.
Keywords: Micro-nano structures, two-photon polymerization, photo-polymerization, two-photon initiator, femtosecond laser, two-photon absorption, nonlinear optics

Introduction

Two-photon polymerization (2PP) has attracted many researchers due to the capability of this unique technique to build 3D structures with resolution beyond the diffraction limit. 2PP is based on two-photon absorption (2PA) in which two photons are simultaneously absorbed by an atom/molecule to excite the system from the lower energy to higher energy state. This nonlinear process was first predicted by Maria Göppert-Mayer in 1931 [1].

Materials used for 2PP are transparent show no linear absorption at the wavelength of the utilized laser. In 2PA process the intensity depletion of the laser beam propagating through the material is proportional to intensity square.

$$\frac{d\,I(z)}{dz} = \alpha_0\, I + \alpha_2\, I^2 \qquad (1)$$

where α_0 is the linear (1PA) and α_2 is the 2PA coefficient. Due to the quadratic dependence of the absorption on the intensity, the amount the absorbed energy would decrease dramatically by distance from the laser beam center. Therefore, only in a small volume around the focal point of the laser beam enough absorption would take place to create a temporal or permanent change in the physical or chemical property of the medium.

The higher the 2PA coefficient, the more effective the medium is. Hence, the 2PA coefficient/cross section of the materials used for 2PA application should be determined. Many techniques have been proposed to determine the 2PA coefficient/cross section within which the Z-scan technique is more popular due to its sensitivity for revealing the nonlinear absorption.

Z-scan technique was first proposed by Sheik-Bahae et al. in 1990 [2]. In the Z-scan experiment, a nonlinear medium is translated along the beam propagation direction through the focus of a tightly focused laser beam while the laser energy transmitted through the sample is measured as a function of the sample position *z*. Far away from the focus the laser beam size is larger thus the intensity is lower and consequently the 2PA is very weak. As the sample approaches the focus the laser beam size becomes smaller thus, the intensity enhances and then the 2PA grows therefore, the energy transmitted through the sample would decrease. As the sample passes the focal point, the inverse process would occur resulting thus in a V-shape transmitted signal as the signature of 2PA. By fitting the theoretical curve (Eq. 2) to the experimental data, the nonlinear absorption coefficient, α_2, could be extracted.

$$T(z) = \sum_{n=0}^{\infty} \frac{(-q_0)^n}{(n+1)^{3/2}\left(1+x^2\right)^n} \qquad (2)$$

where $q_0 = \alpha_2\, L\, I_0$, L is the sample thickness, I_0 is the on-axis peak intensity, x is the dimensionless parameter z/z_0 and z_0 is the Rayleigh length. For solutions it is not meaningful to report the 2PA coefficient since it depends on the concentration. Instead, the 2PA cross section defined in Eq. 3 is determined in GM where 1 GM=10^{-50} $cm^4.s.photon^{-1}.molecule^{-1}$.

$$\sigma = \frac{\hbar\omega\,\alpha_2}{N_A\,\rho\times 10^{-3}} \qquad (3)$$

where $\hbar$ is the reduced Planck constant, N_A is Avogadro's number, and ρ is the concentration in mole per liter.

2PA is the base for many different applications such as two-photon excited fluorescence (2PEF) microscopy [3], two-photon photo-dynamic therapy (PDT) [4], 3D optical data storage [5] and two-photon polymerization (2PP) [6-14]. This nonlinear phenomenon provides 3D visualization, modification and manufacturing in micro scale with nano resolution.

In any 2PA based application, in order to have considerable absorption three parameters are of the most importance. The 2PA coefficient/cross section which can be determined by Z-scan technique, the exposure time which can be controlled by scanning speed and the intensity which itself depends on two variables: the pulse duration and the beam size at the focus. In order to reach the threshold intensity the pulse duration should be too short (usually ps or fs) and the laser beam waist size should also be too small. In 2PP usually a femtosecond laser beam is tightly focused using a high numerical aperture microscope objective inside the resin. The resin is a monomer containing a two-photon initiator (2PI) to trigger the polymerization process. The irradiated PIs inside the focus volume converted to free radicals which are highly active to cross link to a monomer molecule. The produced molecule is still a free radical eager to attach to another monomer molecule creating a longer molecule. In this way the monomer is converted to polymer. However, the polymerization process will stop by some self terminating processes keep the dimension of the polymerized structure below a limit. To build a polymeric structure based on 2PA the laser focus is scanned within the resin by a 3D motorized stage. By scanning the focus in one direction a polymeric line can by produced. The line

width is considered as the resolution of 2PP structures. Sub-micron resolution can easily be achieved. Line width blow 100 nm has also been reported by different groups [14-17] thus, 2PP can be classified as a micro-nano-structuring technique.

Material preparation

The resin used for 2PP is a combination of a monomer and a 2PI. Different 2PIs were investigated by Z-scan technique and examined for 2PP. All 2PIs were synthesized and delivered by Institute of Applied Synthetic Chemistry, Vienna University of Technology. The preparation method can be found elsewhere [18-20].

2PA cross section measurement

In order to determine the 2PA cross section Z-scan technique was employed in two different fashions.

1) Conventional Z-scan: the setup is shown schematically in Fig.1.

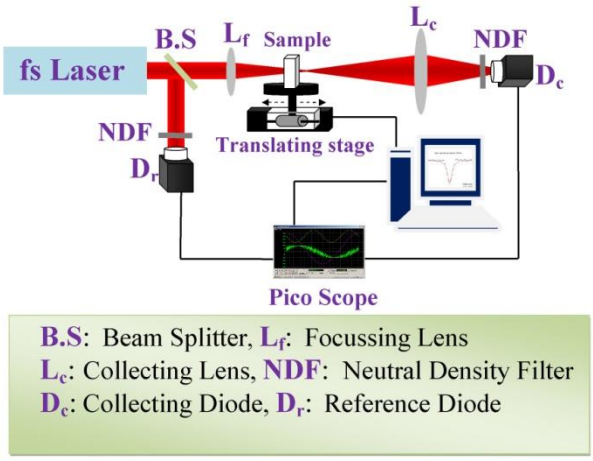

Fig.1. single wavelength Z-scan setup

In our setup a single laser beam is first divided into two parts by a 10/90 % beam splitter. The weaker part is directed toward the reference diode and the stronger one is focused by a 200 mm focal length Plano-convex lens inside the sample. The sample is a 1 mm thick cuvette containing 10 mM concentration of a PI solved in a proper solvent such as methanol (MeOH), tetrahydrofuran (THF) or water. The sample is mounted on a motorized translation stage which translates the sample a few cm through the focus. The energy transmitted through the sample is completely collected by a 60 mm focal length lens and then detected by the collecting diode. The transmittance is measured as the function of sample position. Then, the signal measured by collecting diode is divided by one measured by the reference diode to subtract the laser pulse-to-pulse fluctuation. By fitting Eq. 2 to the measured data and then using Eq. 3 the 2PA cross section can be extracted. It is recommended to repeat the Z-scan for several different intensity/pulse energies to calculate the average and more reliable value for 2PA cross section. Fig. 2 shows the Z-scan data for a PI for different pulse energies. Data points are the experimental data and the solid lines are the fitting curve.

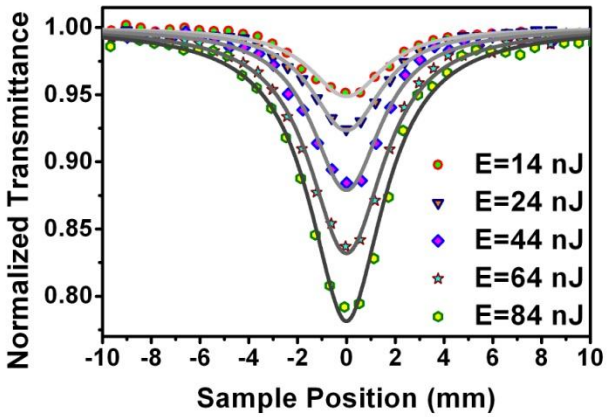

Fig. 2. Z-scans of B3FL 2PI for different pulse energies.

In table 1 the 2PA cross section of investigated 2PIs are summarized.

Table 1. 2PA cross section of investigated 2PI in GM

2PI	M3P	M3K	B3K	M2K	P3K	R1	B3FL
σ	23	165	238	256	261	318	330

2) White light Z-scan: the setup is shown schematically in Fig.3.

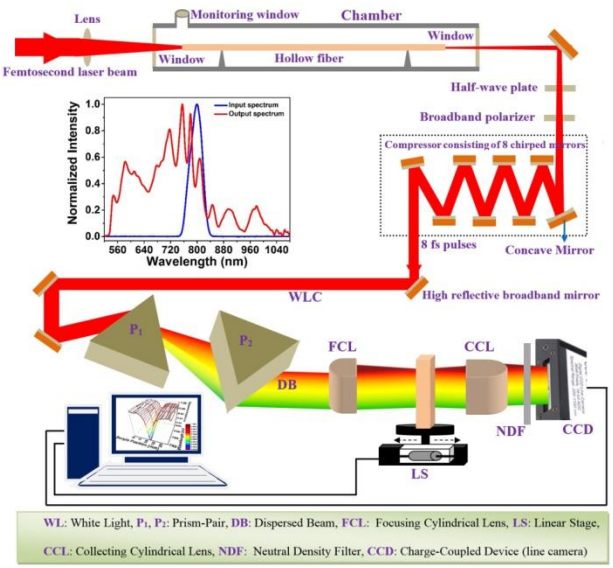

Fig.3. Schematic drawing of WLC Z-scan setup.

In conventional Z-scan technique, the 2PA cross section is obtained for a specific wavelength delivered by the source used for the experiment; that is why it is also called single wavelength Z-scan.

Similar to the linear absorption coefficient, the 2PA is also wavelength dependent. Therefore, it is essential to measure the 2PA spectra to determine the peak 2PA. The wavelength-resolved 2PA spectra are required for tuning the laser to the peak absorption in 2PA-based applications to enhance the efficiency. Additionally, for newly developed compounds the 2PA spectra are essentially necessary as a guide line for designing molecular with higher 2PA cross section. To determine the 2PA spectra a tunable laser or a high intense white light continuum (WLC) source should replace the single wavelength source in conventional Z-scan. We proposed a method to determine the wavelength-resolved degenerate 2PA spectra by performing a single scan using dispersive WLC.

In our setup used for WLC Z-scan (Fig. 3), a compact pro Ti:sapphire laser system was used as a pump source for WLC generation. This system can produce 30 fs, 500 μJ pulses with repetition rate of 1 kHz at central wavelength of 800 nm. The pulses generated by this source are slightly focused using a 150 cm focal length plano-convex lens to a 190 μm diameter spot at the entrance of the 175 cm long hollow fiber mounted on a V-groove holder inside a chamber filled with Ar gas. The inner diameter of the hollow fiber is 250 μm. The chamber itself is mounted on a pair of x-y translation stages. The light guided to the exit of the hollow fiber is spectrally broadened as a consequence of self-phase modulation. The broadband output of the chamber then travels through an ultra-broadband dispersive mirror compressor consisting of 8 chirped mirrors. The pulse duration decreased from 30 fs (for pump pulses) to about 8 fs after the compressor as the pressure inside the Hollow fiber is increased from zero to 0.6 bar. The generated WLC consisting of sub-8 fs pulses was spatially dispersed in horizontal direction and then collimated using a F2-glass prism-pair separated by a distance of 140 cm in a parallel geometry (Fig. 3). The collimated spatially dispersed beam (10 mm height and 30 mm width) was focused by a 150 mm focal length cylindrical lens into a 50 μm high (30 mm wide) line. A cuvette (50 mm height, 50 mm width and 2 mm thick) containing the sample solution mounted on a step-motor translation stage is scanned along the propagation direction of the spatially dispersed focused beam through the focal plane. Since in this method different spectral components of the WLC beam are spatially separated along a narrow horizontal line inside the sample, each infinitesimal volume within the illuminated region of the sample is irradiated with a narrowband (e.g., 10 nm) radiation leading to only degenerate 2PA from the same spectral component. At each *Z*-position the transmitted intensity distribution is then imaged into a charge-coupled device (CCD) line camera (3600 pixels with pixelwidth of 8 μm) using a 50 mm focal length cylindrical lens. The transmittance as a function of sample position measured by each pixel of CCD line camera yields a Z-scan signal for the specific spectral component detected by that pixel. Thus, it is practically feasible to measure 3600 (number of pixels of the camera) Z-scan signals by performing only a single scan. Therefore, the ultimate measured data represent a matrix of *NM* dimension. In this notation *N* denotes the total number of pixels of the CCD line camera (i.e., 3600) and *M* denotes the number of *z*-positions during the entire Z-scan experiment. The 2PA cross section at each wavelength then can be extracted by fitting Eq. 2 to that respective Z-scan detected by a number of pixels of the CCD camera. Figure 4 represents the wavelength-resolved degenerate 2PA spectra of some 2PIs measured by our proposed method.

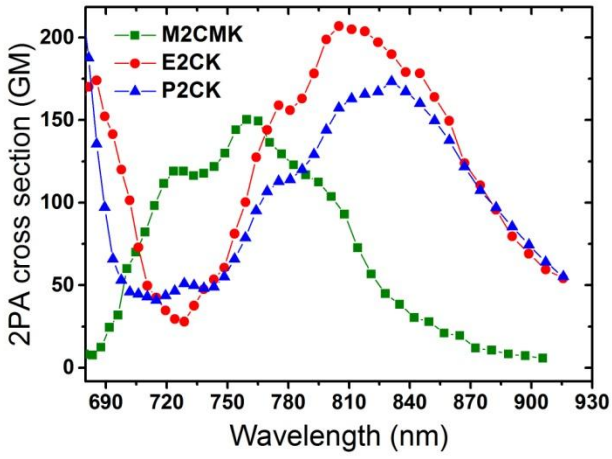

Fig. 4. 2PA spectra of three water soluble 2PIs (M2CMK, P2CK, and E2CK) measured by WLC Z-scan method.

The water-soluble initiator P2CK shows the largest 2PA cross section with the main peak absorption around 810 nm. The second water soluble initiator E2CK has its main absorption peak at 830 nm. M2CMK possess a broad absorption band ranging from 700 nm to 850 nm with the main peak around 760 nm. This information reveals worthful information about the energy states of each molecular structure. By determining the peak absorption, one can now tune the output wavelength of the tunable laser to peak absorption of the 2PI used for 2PP to take advantage of higher scanning speed and thus saving time and expense in 2PP structuring. This is

the most important and applicable result which can be found from the 2PA spectra.

2PP structuring

3D polymeric structures were produced in a solution of the 2PI dissolved in a 1:1 equimolar mixture of trimethylolpropane triacrylate (TTA, Genomer 1330) and ethoxylated- (20/3)-trimethylolpropane triacrylate (ETA, Sartomer 415). The sample is mounted on an assembly of three linear translation stages for complete 3D movement. A tunable femtosecond laser oscillator (MaiTai DeepSee by Spectra Physics) was used for 2PP structuring. The output wavelength can be tuned in the range of 700 nm to 900 nm using an automated dispersive system controlled by computer software. This laser produces 70-80 fs, 25 nJ pulses at repetition rate of 80 MHz. A rotating half wave plate following by a polarizer was used for adjusting the laser beam intensity. Following the polarizer, an acousto-optical modulator was employed for fast switching (on/off) of the laser beam. The laser beam was then broadened using a telescope and finally focused into the sample with a microscopy objective. Different objectives with numerical aperture ranging from 0.4 to 1.2 were employed to optimize the best structure quality along with the highest structural resolution of the 3D structures. The laser beam focus is scanned inside the resin by Galvo-scanner thus any desired real 3D structure can be realized via 2PP. when using high numerical aperture objective the view field is small. Therefore, the large structures are divided into many parts which are built one by one. The Galvo-scanner is used to scan the focus inside the resin to build each sub-divided part and the xy stage is used to move the whole structure to build the next part of the structure.

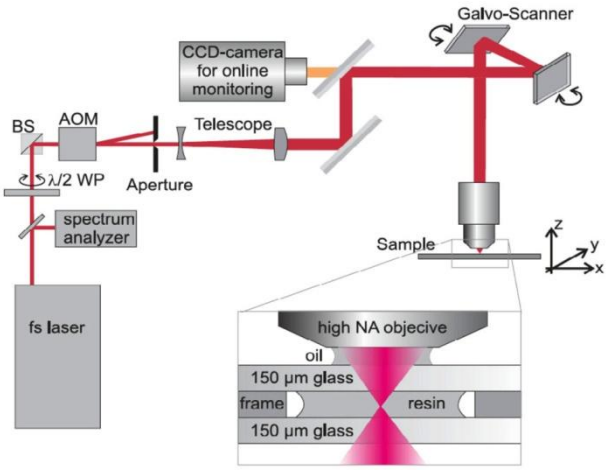

Fig. 5. Schematic drawing of the 2PP machine.

In order to optimize the scanning speed and laser pulse energy a matrix of woodpile structures were created using different speed in the range of 20–200 mm/s and different laser power in the range of 4–22 mW (50-275 pJ pulses) (Fig. 6a and 6b).

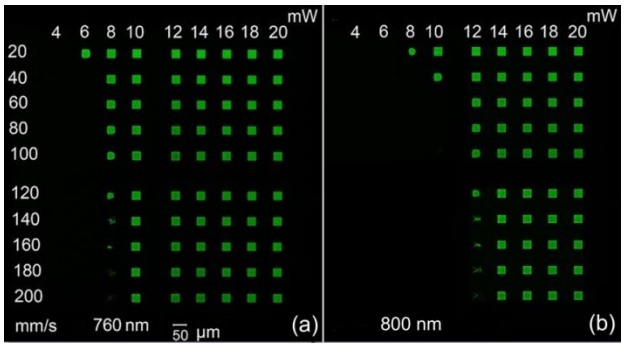

Fig. 6. Laser scanning microscope (LSM) images of the test structures using different writing speed, different laser power and different wavelength.

Structuring test using M2CMK as 2PI showed that at the lowest scanning speed of 20 mm/s, a laser power of 6 mW is sufficient to produce defect-free structures created by 760 nm laser wavelength, whereas 8 mW is still not sufficient to create the same structure using 800 nm. It can be asserted that the power threshold is reduced by more than 20% using 760 nm instead of 800 nm. This observation is in good agreement with the 2PA spectra shown in Fig. 4, explained by the fact that the energy absorbed in the 2PA process is proportional to the product of the 2PA cross section and the square of the laser intensity. Tuning the laser wavelength to match the 2PA peak of M2CMK resulted in a significant increase in the writing speed. By comparison between Fig. 6a and 6b, one can recognize that in the power range of 8–10 mW, the writing speed can be increased by a factor of at least 5 using 760 nm instead of 800 nm. For instance, at a laser power of 10 mW, the scanning speed should be less than 40 mm/s to produce a defect-free structure using 800 nm, whereas the scanning speed can be increased up to 200 mm/s using 760 nm wavelengths. This can be understood because 10 mW is just above the threshold using 800 nm, while for 760 nm, 10 mW is substantially above the threshold and consequently leads to producing much more polymer thus allowing a substantial increase in the scanning speed.

Figure 7 is just as an example to represent the capability and resolution of 2PP structuring. Real 3D structures in micro scale can be created with resolution below 100 nm. This promising technique provides a new and unique means of structuring which has found applications in different area such as optical integrated circuits (IC), tissue engineering and micro devices.

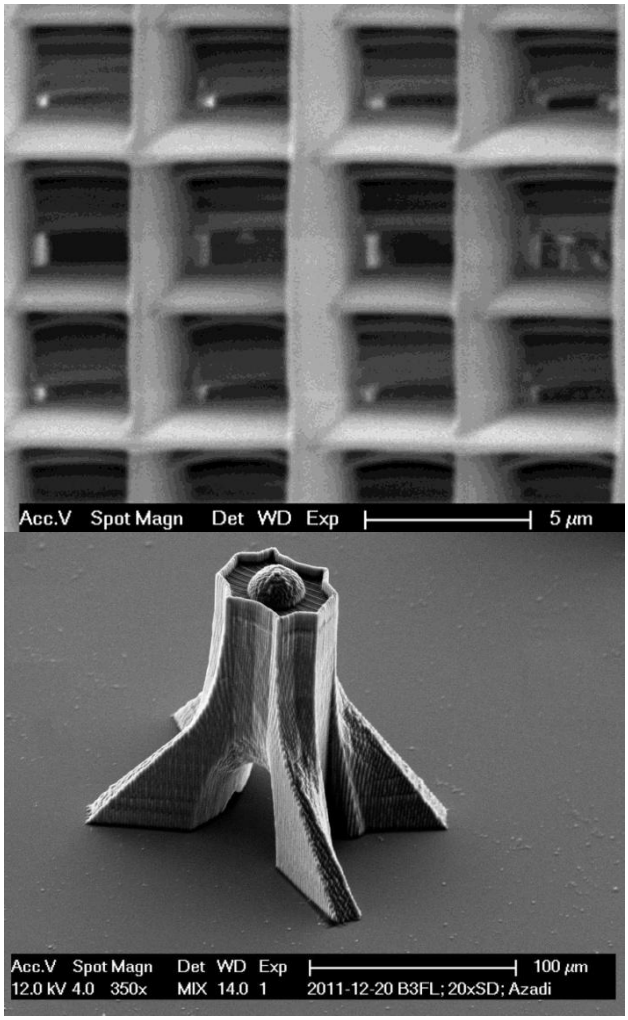

Fig. 7. Woodpile structure and Azadi Tower

Conclusion

In conclusion we reported on the 2PP structuring process including synthesizing the 2PIs, determining the 2PA cross section/spectra and then creating 3D polymeric structuring. Our proposed WLC Z-scan provides means to screen the spectral 2PA characteristics of different compounds in a quick and reliable manner.

The results obtained from 2PA spectra and 3D structuring, which is returned to the chemistry researchers, can serve as a guideline and establishing a protocol for the design of specialized 2PIs in order to synthesize new molecule structures with higher 2PA cross section.

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