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Two-photon absorption: from optical power limiting to 3D microfabrication

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Abstract

We report here recent results obtained in the field of molecular engineering for two-photon absorption (TPA); this paper deals with two specific applications: optical limiting in the visible range and microfabrication. The nonlinear absorption and optical power limiting properties of a conjugated system (fluorene) and polyfluorenes induced by TPA, were performed in the visible range for nanosecond time duration pulses. The TPA cross-section of small oligomers increases with the square of their lengths: this trend is rationalized in terms of excitonic coupling between monomers within the range of the effective length of the oligomer. We also report on the characterization of efficient photoinitiators for radical polymerization at 532 and 1064 nm by TPA. Symmetric molecules optimized for TPA and for optical limiting properties with a $D-\pi-D$ structure (bearing tertiary amines as a donor group D and a biphenyl or a fluorene for the transmitting π electron group) were proposed for the visible. In the infrared, the selected photoinitiators present the general structure $D-\pi-A-\pi-D$, in which A is an acceptor group. The initiation efficiencies of these systems were evaluated by the determination of the threshold intensities for a given exposure duration. Compared to the commercial resins for UV photopolymerization and generally involved in TPA, these optimized initiators led to a significant increase of the sensitivity during fabrication. Weaker incident intensities and faster scanning speeds could be used. This approach allows the fabrication of three-dimensional micro-objects with a low cost nanosecond pulsed microlaser. **To cite this article:** G. Lemerrier et al., C. R. Chimie 8 (2005).

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Résumé

Nous présentons quelques résultats récents dans le domaine de l'ingénierie moléculaire pour l'absorption à deux photons (ADP) ; cet article concerne plus particulièrement deux applications : la limitation optique et la microfabrication d'objets 3D. L'absorption non linéaire et les propriétés de limitation optique induite par ADP du fluorène et de polyfluorènes ont été étudiées dans la gamme spectrale du visible et en régime nanoseconde. La section efficace d'absorption à deux photons de petits oligomères augmente avec le carré de leur longueur ; cette tendance est rationalisée en termes de couplages excitoniques entre

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monomères dans la limite d'une longueur effective des oligomères. La caractérisation de photoinitiateurs efficaces en polymérisation à 532 et 1064 nm par absorption à deux photons est également reportée. Des molécules symétriques de structure $D-\pi-D$ (portant une amine tertiaire comme groupement donneur D et un biphenyle ou un fluorène comme groupe transmetteur π) optimisées pour l'ADP et les propriétés de limitation optique sont proposées pour le visible. Pour l'infrarouge, les photoinitiateurs sélectionnés sont de structure générale $D-\pi-A-\pi-D$, dans laquelle A est un groupe accepteur. L'efficacité d'initiation de ces systèmes a été évaluée par la détermination d'une intensité seuil pour une durée d'exposition donnée. Par comparaison avec les résines commerciales pour la photopolymérisation UV et généralement utilisées pour l'ADP, ces initiateurs optimisés conduisent à une augmentation significative de la sensibilité pendant la fabrication de micro-objets tri-dimensionnels avec un laser nanoseconde peu onéreux. **Pour citer cet article : G. Lemerrier et al., C. R. Chimie 8 (2005).**

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Keywords: Two-photon absorption; Fluorene oligomer; Optical power limiting; Excitonic coupling; Microfabrication; Photopolymerization initiators

Mots clés : Absorption à deux photons ; Oligofluorène ; Limitation optique ; Couplage excitonique ; Microfabrication ; Initiateurs de photopolymérisation

1. Introduction

Irradiated by intense laser pulses, organic molecules can absorb two photons simultaneously; the probability of the two-photon absorption (TPA) phenomenon is proportional to the square of the laser intensity. In organic materials, TPA is a well-known process involved in a lot of different applications [1] for three-dimensional (3D) optical data storage [2], 3D-fluorescence imaging [3], photodynamic cancer therapy [4], optical limiting [5–8], and microfabrication [9–11]. This work concerns molecular engineering for the last two fields.

2. Optical power limiting in the visible range

2.1. General

A lot of investigations focusing on optical limiting materials, for the protection of eyes and optical systems against tunable lasers, have already been reported [12]. The materials involved require high transmission at low irradiance, but a large nonlinear absorption at damageable fluences. Efficient nonlinear absorbers, based on a TPA process, were designed [6,13,14]; this was considered as a very attractive approach due to the instantaneous response and the lack of saturation in highly concentrated materials. Concerning the optical limitation effect on nanosecond time scales, a further level has been reached by the occurrence, in the non-

linear absorption, of an excited-state absorption (ESA) process [13–19]. This three-photon absorption process can be described by two steps during the nanosecond pulse duration: an instantaneous TPA step followed by a very fast relaxation to the lowest excited-state and the ESA process. From the phenomenological point of view, this optical limiting behavior can be described, according to Eq. (1), in which z is the propagation direction and I the beam intensity:

$$\frac{dI}{dz} = -\alpha_1 I - \alpha_2 I^2 - \alpha_3 I^3 \quad (1)$$

In experimental conditions (transparency of materials at laser wavelengths), $\alpha_1 \approx 0 \text{ cm}^{-1}$ and $\alpha_2 I^2 \ll \alpha_3 I^3$ (under conditions of high intensity). When the lifetime τ_{01} of the lowest excited-state is shorter than the pulse duration, the phenomenological three-photon absorption coefficient α_3 can be written, in the case of singlet-singlet transition, as follows (2):

$$\alpha_3 = \frac{N \sigma_{\text{TPA}} \sigma_{\text{ESA}} \tau_{01}}{V 2(\hbar\omega)^2} \quad (2)$$

where σ_{TPA} , σ_{ESA} are, respectively, the TPA and ESA cross-sections; N/V is the concentration and ω the laser frequency. The optimization of α_3 requires the simultaneous optimization of all parameters involved in Eq. (2) (σ_{TPA} , τ_{01} and σ_{ESA}) with, in addition, a broad spectral overlap between TPA and ESA properties. For centrosymmetric molecules, the cross-section σ_{TPA} is usu-

ally described by the three-level model following the relationship (3) [20]:

$$\sigma_{\text{TPA}} \propto \frac{\mu_{01}^2 \mu_{12}^2}{\left(E_{01} - \frac{E_{02}}{2}\right)^2} \quad (3)$$

where μ_{01} , and μ_{12} are the transition moments between the ground state S_0 and the lowest charge transfer excited-state S_1 (at energy E_{01}), and between S_1 and the lowest two-photon excited-state S_2 (at energy E_{02}), respectively. The most frequently used strategy employs centrosymmetric molecules constituted by a delocalized π electron system substituted at each end by donor groups [7,20–22]. The best approach to optimize σ_{TPA} values was shown to be to increase the charge transfer system within molecules [20,23]. This approach led to giant values of cross-sections with, however, the TPA spectra shifted towards IR, incompatible with applications in the visible range.

2.2. Experimental section

The TPA experimental set-up has already been presented elsewhere [8,24]. A Nd–YAG laser, pumping an optical parametric oscillator (OPO) and producing 2.6 ns pulses (with 10 Hz repetition rate) in the range of 450–650 nm, was used. TPA excitation spectra were recorded from fluorescence collected at 90° of the incident beam. Calibration of TPA spectra was performed from *p*-bis(*o*-methylstyryl)benzene as a standard [25,26] in order to scale two-photon excited fluorescence spectra and the pulse energy was kept low enough to ensure a quadratic dependence of the fluorescence signal on input energy. The ESA cross-section and decay time were measured from Kerr ellipsometry experiments as previously described [22]. The signals which, when observed for “long” delays (500 ps)

between pump and probe beams, presented the same absorption profiles as those obtained in the zero delay, could be assigned to S_1 – S_n absorption. The three-photon coefficient α_3 was obtained from nonlinear transmission measurements, as described in Ref. [8], by using relationship (4), where L is the sample thickness:

$$T_E = \iint \frac{1}{\sqrt{1 + 2\alpha_3 L I^2(r, t)}} dr dt \quad (4)$$

Nonlinear transmission data were measured at constant laser fluence, by wavelength scanning of the collimated beam (210 μm HW1/e²M) of the OPO laser system.

2.3. Results and discussion

A molecular engineering work to design efficient two-photon absorbers from N^4, N^4 -bis-(4-methoxyphenyl)- N^4, N^4 -diphenyl-4,4'-diaminobiphenyl (**1**) (Fig. 1), for optical limiting in the visible range, was performed [27], by optimization of σ_{TPA} values or dynamics of excited-state.

Molecule **1** belongs to the large tetraphenyl diamine (TPD) family, which is currently used in organic luminescent diodes as hole injection layers [28,29] and is generally considered to be thermally stable. The molecular structure of **1** presents a D – π – D structure (in which D is a donor group) with moderate charge transfer character (for an efficiency in the visible range) due to the non-planarity of the biphenyl. Two strategies for **1** were considered in order to optimize α_3 (Eq. (2)), allowing in each case, the use of an aminobiphenyl type substituent as the donor group while keeping transparent molecules (λ_{max} between 349 and 374 nm): (a) the optimization of the charge transfer by increasing the system planarity (molecule **2**, in where the biphenyl

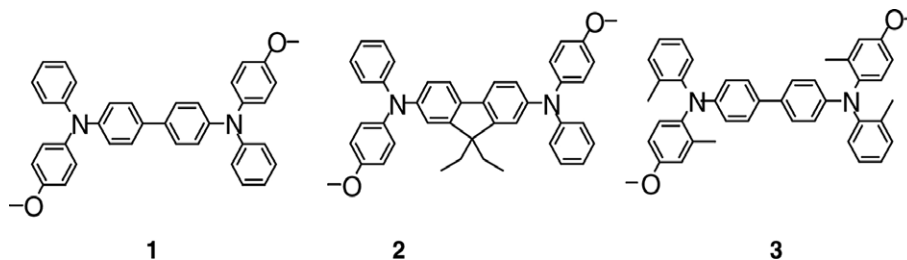


Fig. 1. Molecular structures of 1–3.

was replaced by a fluorene) in order to boost the TPA cross-section σ_{TPA} (from $40 \times 10^{-50} \text{ cm}^4 \text{ s}^{-1}$ photon per molecule—or 40 G.M. for Göppert–Mayer—for **1** to 100 G.M. for **2**, see coefficients Table 1); leading, according to relationship (2), to better nonlinear absorption properties ($\alpha_3 = 7950 \text{ cm}^3 \text{ GW}^{-2}$ at 500 nm for **2** vs. $3900 \text{ cm}^3 \text{ GW}^{-2}$ at 550 nm for **1** as reported in Table 1); (b) the optimization of the excited-state dynamics in order to slow down the relaxation processes and increase the value of τ_{01} which is also a relevant parameter in the expression of the three-photon absorption coefficient α_3 (Eq. (2)).

Molecule **3** (Fig. 1), which presents identical charge transfer properties as molecule **1**, leads to a similar TPA efficiency. However, when molecule **3** possesses methyl substituents on the peripheral rings which hinder their free rotation, nonradiative de-excitation processes decrease and the lifetime of the lowest excited-state increases compared to that of **1** ($\tau_{01} = 360 \text{ ps}$ for **1** and 420 ps for **3** as reported in Table 1); moreover, the ESA cross-section ($\sigma_{\text{ESA}} = 1.8 \times 10^{-16} \text{ cm}^2$ for **1** and $3.8 \times 10^{-16} \text{ cm}^2$ for **3**) induces a net increase in the nonlinear absorption properties ($\alpha_3 = 9000 \text{ cm}^3 \text{ GW}^{-2}$ at 535 nm for **3** and $\alpha_3 = 3900 \text{ cm}^3 \text{ GW}^{-2}$ at 550 nm for **1**), with similar σ_{TPA} . A new approach involving unsubstituted oligomers, such as Stilbene 3 (a bistilbene) [17] or polyfluorenes derivatives [8,24], appears very promising in terms of TPA cross-sections in the visible range. In the light of the encouraging preliminary results from Stil-

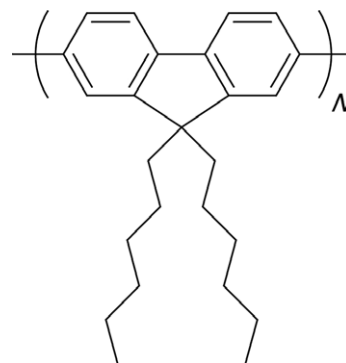


Fig. 2. Chemical structures of *N*-PDHF oligomers.

bene 3, which presents α_3 values larger than $10,000 \text{ cm}^3 \text{ GW}^{-2}$, a study of *N*-poly(9,9-dihexyl-fluorene-2,7-diyl) (*N*-PDHF, as shown in Fig. 2) selected for their high photochemical stability was performed in solution as a function of the molecule length (monodispersed [8,24,30] systems and polydispersed for the longest molecules).

A red shift of the linear absorption maxima of *N*-PDHF (in chloroform) is observed as a function of the length of the oligomer (Table 2); nevertheless, all molecules are transparent in the visible range.

The three-photon absorption coefficient α_3 presents high values at resonance for the longest oligomers [31] ($\alpha_3 = 100,000 \text{ cm}^3 \text{ GW}^{-2}$ for $N = 60$ at a concentration of 200 g l^{-1}) compared to other organic molecules such as symmetrically substituted molecules [22] which

Table 1
Experimental TPA, ESA $S_1 \rightarrow S_n$ and nonlinear absorption properties of molecules 1–3

Compound	1	2	3
$\lambda_{\text{max}}/\text{nm}$	350	374	349
$\sigma_{\text{TPA}}/10^{-50} \text{ cm}^4 \text{ s}$ per photon per molecule	40	100, 120	30, 35
($\lambda_{\text{TPA}}/\text{nm}$)	(550)	(550, 640)	(550, 585)
$\sigma_{\text{ESA}}/10^{-16} \text{ cm}^2$	1.8	1.4	3.8
($\lambda_{\text{ESA}}/\text{nm}$)	(545)	(585)	(545)
τ_{01}/ps	360	320	420
$\alpha_3/\text{cm}^3 \text{ GW}^{-2}$	3900, 2000	7950, 2500	9000, 6000
(λ_3/nm)	(550, 610)	(500, 625)	(535, 585)

Table 2
Optical properties of *N*-PDHF

N	λ_{max} (nm)	λ_{TPA} (nm)	σ_{TPA} ($10^{-50} \text{ cm}^4 \text{ s}$ photon per molecule)	α_3 ($\text{cm}^3 \text{ GW}^{-2}$)
2	330	540	55	5000
4	364	602	600	/
16	373	620	4000	10 000
25	382	620	9000	30 000
60	388	620	20 000	100 000

exhibit α_3 values weaker than $10,000 \text{ cm}^3 \text{ GW}^{-2}$ measured in the same exact conditions; this lead to efficient optical power limiting in the whole visible range (the maximum transmitted energy being lower than $10 \text{ }\mu\text{J}$ for an input energy of up to $350 \text{ }\mu\text{J}$ in a F/5 optical geometry).

TPA wavelength maxima and cross-sections are reported in Table 2. The TPA cross-sections of small oligomers increase with the length squared. This trend is rationalized in terms of excitonic coupling between monomers within the range of the effective length of the oligomer. Large TPA values, when compared to those of the substituted biphenyls **1–3** (see Table 1) optimized for the visible range, were obtained for the longest oligomers, which present a TPA efficiency of the order of $100 \times 10^{-50} \text{ cm}^{-4} \text{ s photon per molecule}$ (100 G.M.). However, the most relevant parameter allowing to rationalize the TPA efficiency of oligomers is the cross-section density (TPA/ N) which permits to overcome concentration effects due to the increase of the number of monomer units and to really determine the influence of the length of the oligomer. The values of this parameter for various N are reported in Fig. 3 and can be readily analyzed from the excitonic interaction model proposed to interpret high TPA cross-sections of this oligomer family [32,33].

This coherent coupling of transition dipole moments between monomers (similar to that observed for J -aggregates [34]), induces a power law variation between transition dipole moment of the oligomer N

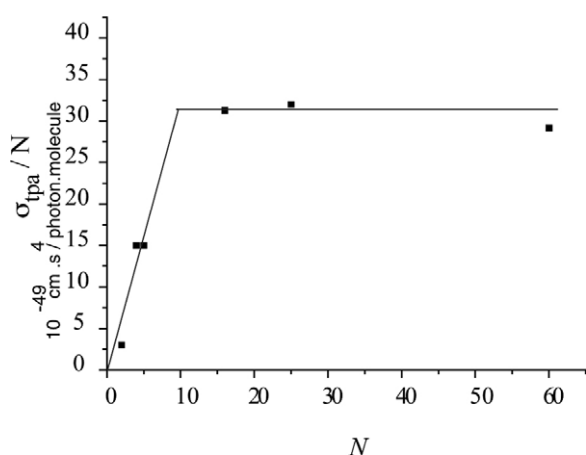


Fig. 3. TPA cross-section density of N -PDHF with the length of the oligomer.

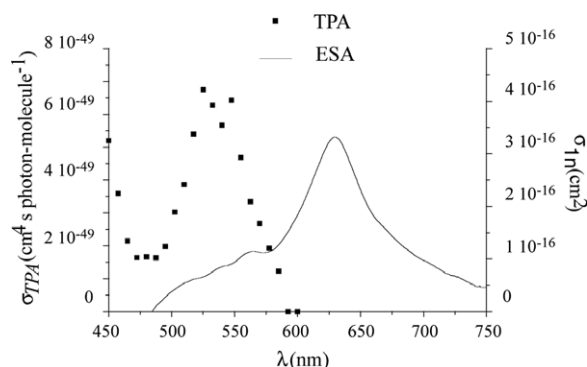


Fig. 4. TPA-ESA overlap for 2-PDHF.

and that of the monomer for the $i \rightarrow j$ transition, following Eq. (5).

$$\mu_{ij}(N) \approx \sqrt{N} \mu_{ij}(1). \quad (5)$$

An analytical interpretation based on the three-level model (Eq. (3)) and treating the excitonic type coupling between oligomers as a perturbation, seems to corroborate this assumption [35].

However, as illustrated by Fig. 4 for 2-PDHF, TPA and ESA resonances do not overlap efficiently for this family of compounds [8]; this observation allows to assume that further optimization of α_3 properties could be expected.

Further work is needed to find derivatives showing an improved overlap and therefore a larger optimized nonlinear response; in that perspective, 2D and/or 3D dendrimers of fluorenes could be of great interest in the design of molecules in order to increase the excited-state level density and enhance TPA cross-sections (i.e. efficient optical power limiting properties).

3. 3D microfabrication

3.1. General

TPA induced photopolymerization is a very promising method for the fabrication of 3D microstructures [9,11,36–40]. The chromophore acting as the photoinitiator is excited by the simultaneous absorption of two photons leading to chemical polymerization reactions; due to a tight confinement of the excitation volume around the focal point, this method can produce micrometer sized and highly resolved objects. This TPA

based technique led recently to the production of optical devices [41], optical storage [10], photonic bandgaps [42,43] and micromachines [44]. However, high laser intensities and long exposure durations were required due to the use of commercial UV photoinitiators with weak TPA efficiencies. These works were performed using onerous femtosecond Ti: sapphire lasers at intensities close to the damage thresholds of the materials. These operating conditions are a major drawback to the widespread utilization of this promising technique of fabrication. In this context, a molecular engineering work to improve TPA photoinitiators was needed in order to use cheaper lasers with lower peak powers. The 3D microfabrication by TPA polymerization employing a new efficient photoinitiator and using a low cost microlaser has recently been demonstrated [45]. The symmetrically substituted fluorene **2** was used to initiate TPA polymerization of acrylates in the visible range at 532 nm; molecule **2** presents a high TPA efficiency in the visible, as demonstrated above, with substituents able to produce free radicals, as required by the initiation step as shown in Fig. 5.

New conjugated ketones **5–7**¹ (Fig. 6) with a molecular structure similar to that of the Michler ketone [46] **4**, were presented for the IR photoinitiation at 1064 nm.

The oxidation potential, reported in Table 3, is also a relevant parameter for the characterization of the photopolymerization process since a mono-electronic transfer from the initiator to the acrylate monomer is required; the low values obtained for these electron rich

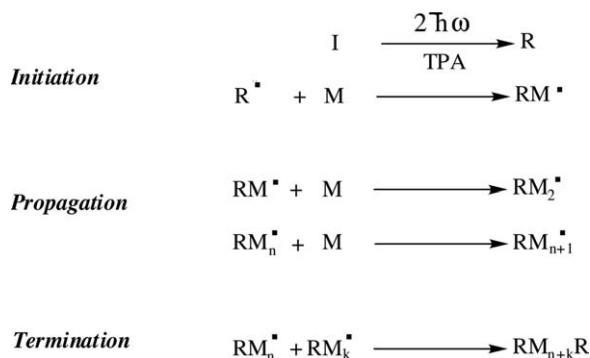


Fig. 5. Different steps in a radical photopolymerization reaction. I represents an initiator molecule, R is a radical and M a monomer.

photoinitiators, show the ability for both molecules to give an electron from the donor group and create a radical.

3.2. Experimental section

As described above, TPA spectra of compounds **5–7** were obtained (Table 3), in the 780–1120 nm range; TPA cross-section at 1064 nm were determined using Rhodamine B as a standard [47] in order to scale the two-photon excited fluorescence spectra and are reported in Table 3. All TPA induced photopolymerization experiments at 532 nm were performed using a frequency doubled Nd–YAG Nanolase microlaser from JDS Uniphase ($\lambda = 532$ nm, 0.5 ns pulse duration, 4 μJ maximum pulse energy, 6.5 kHz repetition rate) focused

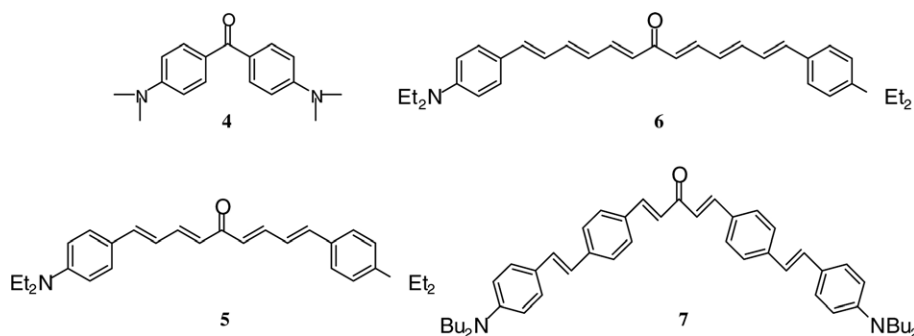


Fig. 6. Molecular structures of **4–7**.

¹ Synthesis will be published elsewhere.

Table 3

 σ_{TPA} , E_{pa} and I_{min} values for molecules 2, 5–7

Photoinitiator	Weight (%)	σ_{TPA} (cm ⁻⁴ s)	$\lambda_{\text{irradiation}}$ (nm)	E_{pa} (mV) vs. $E_{\text{Fc}}+I_{\text{Fc}}$	I_{min} (W m ⁻²) for $t_{\text{expo}} = 10$ ms (laser wavelength in nm)
2	3	80×10^{-50} (532)		/	1.4×10^{14} (532)
2	0.5	80×10^{-50} (532)		+250	2.8×10^{14} (532)
5	0.5	50×10^{-50} (1064)		+260	8.7×10^{14} (1064)
6	0.5	100×10^{-50} (1064)		+170	5.1×10^{14} (1064)
7	0.5	65×10^{-50} (1064)		+170	3.9×10^{14} (1064)

through a $\times 5$ objective lens; for 1064 nm experiments, the Nd–YAG Nanolase microlaser produced pulses with a duration of 0.64 ns, a maximum energy of 5.4 μJ , and a repetition rate of 13.6 kHz focused through a $\times 40$ objective lens with a numerical aperture (NA) of 0.75. The films were placed on a three axis piezoelectric stage allowing their translation relative to the laser focal point. The resins consisted in 0.5–3% photoinitiator, 70% monomer (tris(2-hydroxyethyl) isocyanurate triacrylate with a radical inhibitor level of 100 ppm) and 27–30% polymer binder (poly(styrene-co-acrylonitrile) (75/25)). Films with a thickness of between 20 and 50 μm were obtained by solvent evaporation from a chloroform solution.

The initiation efficiencies of these systems were evaluated [48] by the determination of the threshold intensities for a given exposure duration. The incident intensity distribution, which is assumed to be Gaussian, determines the shape of the polymerized volume. Using the microlasers at 532 or 1064 nm, several studs of polymer were fabricated in the resin. Fig. 7 presents an image of a typical stud from the scanning electron microscope; the studs, which can be compared to a rota-

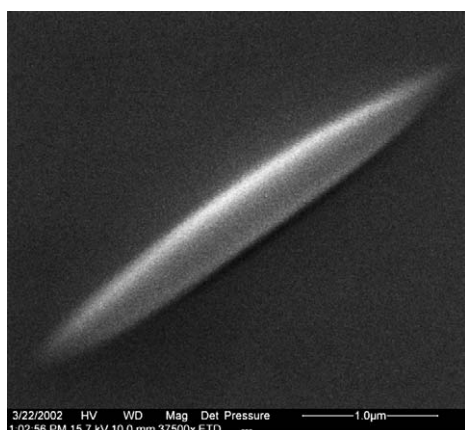


Fig. 7. Scanning electron microscope image of a stud lying on the glass substrate after dissolution with acetone.

tion ellipsoid with their long axis corresponding to the focal axis of the laser beam, lie down on the glass substrate during the dissolution of polymerized areas in acetone.

The threshold intensity inducing polymerization I_{min} , can be assessed from the intensity associated to the edge of the polymerized volume (Fig. 8).

The value of I_{min} is given by Eq. (5), where W is the stud width (polymerized volume) and ω_0 the beam waist.

$$I_{\text{min}} = I_0 e^{-\frac{2(W/2)^2}{\omega_0^2}} \quad (5)$$

For incident intensities $I_{\text{inc}} < I_{\text{min}}$, the polymerization is not sufficient to induce a significant change in the resistance to dissolution.

3.3. Results and discussion

Results were analyzed for exposition time $t_{\text{expo}} = 10$ ms (see Table 3) comparing data obtained for molecule 2 at 532 nm and molecules 5–7 at 1064 nm.

The comparison of the data for molecule 2 at 3.0% or 0.5% shows that, as expected, a lower concentration

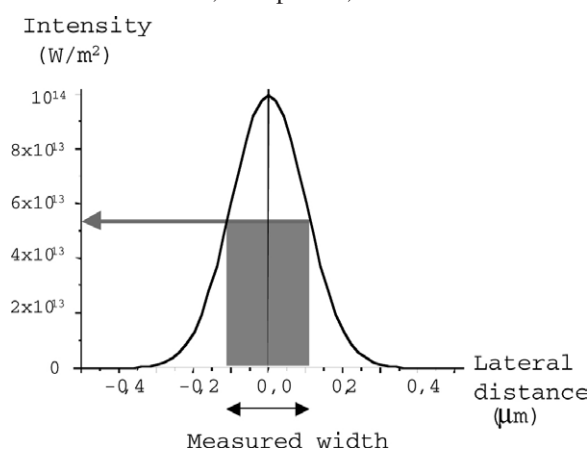


Fig. 8. Determination of the polymerization threshold intensity.

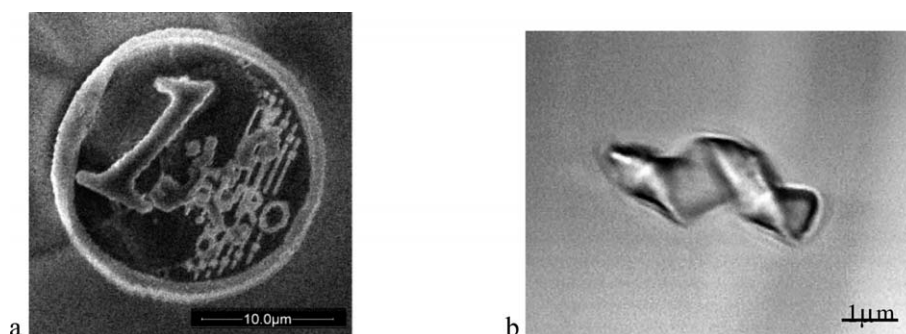


Fig. 9. Two fabricated micro-objects: (a) a micro Euro coin and (b) a micrometer sized Archimedes' screw.

leads to a lower sensitivity. Although both molecules present similar TPA properties, photoinitiators **5–7** designed for IR are less sensitive than **2** designed for visible light. Comparing to the commercial resins for UV photopolymerization generally involved in TPA, these optimized initiators led to a significant increase of the sensitivity during fabrication.

This work provides a quantitative study of the TPA induced polymerization efficiency and allows us to compare different photoinitiators. However, values of threshold energies represent the global initiation efficiency of molecules: (1) their TPA efficiency, (2) their ability to create radicals which (3) will react with the monomer to induce the polymerization, while value of the TPA cross-section reflects only the efficiency of molecules to induce the first step of the initiation stage.

4. Conclusion

This paper summarizes a wide range of work on engineering and characterization of TPA chromophores, targeting optical limiting in the visible and 3D micro-fabrication applications. A same molecule, adequately substituted can be used efficiently for both applications.

For optical limiting in the visible range, the oligomer approach based on excitonic interactions opened a new way to enhance the TPA efficiency, leading to promising nonlinear absorption responses. The study of different dendritic systems to optimize this response through ESA properties is in progress [49,50].

3D micro-objects can be prepared by TPA based photopolymerization: a 20 μm diameter Euro coin [45] and a micrometer-sized Archimedes' screw are presented in Fig. 9. The design of efficient TPA initiators at

532 and 1064 nm have allowed to use weak power microlasers making this promising technique viable for industrial applications. From this point of view, the study of 3D micro-rotors controlled by optical tweezers is in progress under various conditions of power laser and rotation speed [51].

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