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Two-photon absorption cross-sections of common photoinitiators

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Abstract

Recent interests in and applications of two-photon absorption (2PA) induced photopolymerization have afforded advanced opportunities to perform three-dimensionally resolved polymerization, resulting in intricate microfabrication and imaging. Many of the reported 2PA-induced polymerizations make use of commercially available photoinitiators, and a key parameter to consider is the two-photon absorption cross-section (δ) of the initiator. To date, there has been no comprehensive investigation of two-photon absorptivity of commercial photoinitiators, though a few studies presenting novel photoinitiators for two-photon polymerization have appeared. Herein, we report the 2PA properties of common, commercially available photoinitiators typically utilized in conventional radiation curing science and technologies, and often used in 2PA-based polymerizations. Z-scan and white-light continuum (WLC) pump–probe techniques were utilized to obtain two-photon absorption cross-sections (δ). The results for most compounds were found to yield good agreement between the two methods. Most of the photoinitiators studied possess low δ, except Irgacure OXE01, indicating a need for the development of new photoinitiators with improved properties optimized for 2PA applications. A compound prepared in our laboratories exhibits high 2PA and was useful as a two-photon free-radical photoinitiator.
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1. Introduction

The process of two-photon absorption (2PA), applied to photopolymerization, is a method being examined for a number of advanced applications such as the production of intricate three-dimensional (3D) microstructures [1–3], high density optical data storage [4], and 3D integrated optical components [5–7]. Typical resins used for photopolymerization are often comprised of carefully selected photoinitiators, monomers and/or oligomers, photosensitizers or co-initiators, and various additives may often be included in the final composite system. Inherent in these photopolymerizable resin systems is the use of photoinitiators typically absorbing UV and/or visible radiation. Efforts in the synthesis and photochemical studies of novel photoinitiators with more desirable properties have been the subject of investigation for conventional UV-visible radiation curing technologies [8,9]. Conventional photoinitiators, however, often suffer from small 2PA cross-sections (δ) in the near-IR

wavelength range where femtosecond-lasers are typically used for 2PA-induced polymerization. Previously reported δ values for a limited number of conventional photoinitiators are on the order of or less than 10 Göppert Mayer (GM) units, where $1\,\text{GM} = 10^{-50}\,\text{cm}^4\,\text{s}$ per photon [3]. Despite the low δ values, we have demonstrated the general utility of a wide variety of conventional photoinitiators for the 2PA polymerization of acrylate, epoxide, vinyl ether, and thiol-ene monomers [10–12].

In response to the low δ of commercially available photoinitiators, efforts have been made to prepare novel photoinitiators possessing higher 2PA cross-sections, with the expectation that larger δ values allow for lower laser powers and shorter irradiation time, resulting in minimal optical damage to materials [3,10,13]. It has also been suggested that a photoinitiator possessing high δ may allow the use of low-cost micro-lasers, of the same polymerization speed as that obtained with conventional femtosecond-lasers and commercial UV resins [14].

Efforts to produce novel photoinitiators with improved photosensitivity to near-IR radiation for 2PA polymerization are limited, and subject to tedious synthetic procedures.

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Development of better 2PA photoinitiators would be expected to impact 3D photopolymerization technologies, but such compounds are not currently commercially available. As such, many 2PA-induced polymerizations directed towards micro- and optical-component fabrication continue to employ conventional, commercially available UV-visible photoinitiators. Additionally, previous 2PA microfabrication efforts using commercial UV resins and photopolymerizable systems reveal little information pertaining to the photophysical properties of the photoinitiators used [1,2,5].

To date, there has been no comprehensive investigation of the two-photon absorptivity of commercial photoinitiators. As these initiators are in current and continual use, information on their 2PA properties may facilitate optimization of 2PA-induced polymerization conditions. In this paper, we report on a study of the 2PA properties of several common, commercially available photoinitiators using two complementary non-linear transmission spectroscopic methods. Many of these initiators undergo the Norrish type I α-cleavage reaction involved in radical generation, and include α-hydroxyketones, α-aminoketones, and acylphosphine oxides. Additional initiators studied include a metallocene, an iodonium salt photoacid generator (PAG), the commonly used aryl ketone initiator isopropylthioxanthone (ITX), along with two newer materials (CIBA Specialty Chemical Corp.). The δ value of a strong two-photon absorbing compound (DPABz), previously demonstrated as an effective initiator for acrylate polymerization under 2PA excitation conditions [10], is also presented for comparison.

2. Experimental

2.1. Sample preparation

The following photoinitiators were used as received from CIBA Specialty Chemicals Corp.: Irgacure series 184, 261, 369, 651, 754, 819, 907, and OXE01; and Darocure series TPO, MBF, and 1173. Isopropylthiozanthene-9-one (ITX) was purchased from Sigma–Aldrich and was recrystallized twice in $MeOH/CH_2Cl_2$ prior to use. [4-[2-(Hydroxytetradecyl)oxy]phenyl] phenyliodonium hexafluoroantimonate (CD1012) was purchased from Sartomer and used as received. All commercially available photoinitiators were dissolved in MeOH (Sigma–Aldrich, HPLC grade), and their linear UV-visible absorption spectra collected on a Cary 500 spectrophotometer. The concentrations used for the linear absorption measurements were approximately, 1.0×10^{-6} M. The synthesis and linear spectroscopic properties of the compound (7-benzothiazol-2-yl-9,9-bis-decyl-fluoren-2-yl)-diphenyl-amine (DPABz) have been thoroughly characterized and reported [15,16]. All photoinitiators were prepared as 1.0×10^{-2} M solutions for their 2PA characterization.

2.2. White-light continuum pump–probe technique

Two non-linear transmission techniques were used to measure the 2PA properties of the photoinitiators. The source used for these two methods was a Ti:sapphire-based laser system (CPA-2001, CLARK-MXR) which provided laser pulses of 150 fs duration at 775 nm at a 1 kHz repetition rate. This laser in turn pumped two identical optical parametric amplifier (OPA) systems (TOPAS, Light Conversion) which could produce pulses of 110–150 fs over a broad range in the near-IR and/or visible.

The first method employed a femtosecond white-light continuum (WLC) pump–probe non-linear spectrometer. In this experimental set-up, one OPA provides a strong pump beam which induces a non-linear response in the system under investigation and the other OPA generates a weak, broad-band WLC beam which probes the induced non-linearity. The WLC is generated by focusing 1–2 μJ of 1300 nm light into a 2 mm thick piece of calcium fluoride. The 2PA process requires simultaneous absorption of one photon from both the pump and probe beams and the outcome is the non-degenerate 2PA spectrum of the sample. It is the broad bandwidth of the WLC probe that allows us, in principle, to measure the full 2PA spectrum in a single-shot. However, in practice, the creation of the WLC imposes temporal chirp on the probe beam, which requires us to delay the pump pulse with respect to the probe pulse in order to obtain the entire 2PA spectrum. By correcting for this temporal chirp and accounting for linear propagation effects, we can effectively characterize a sample's 2PA spectrum. A full description of this method can be found in [17].

2.3. Z-scan technique

The second method utilized to measure the 2PA properties of the photoinitiators was the Z-scan technique. In this experiment, the transmittance of a focused beam is monitored after passage through the sample under investigation [18]. The sample is translated along the axis of a focused beam and passes through the waist of the beam where the irradiance is at a maximum and hence, provided the sample exhibits 2PA, the transmittance of the beam should be at a minimum. Fitting this transmittance versus sample position allows δ to be extracted. By repeating this experiment for various pump-wavelengths, determination of the full-degenerate 2PA spectrum can be made. Furthermore, although each method described above has its own benefits, our choice for employing both methods was to provide further confidence in the end results.

3. Results and discussion

The structures and the linear UV-visible absorption spectra (in MeOH) for all the photoinitiators studied are shown
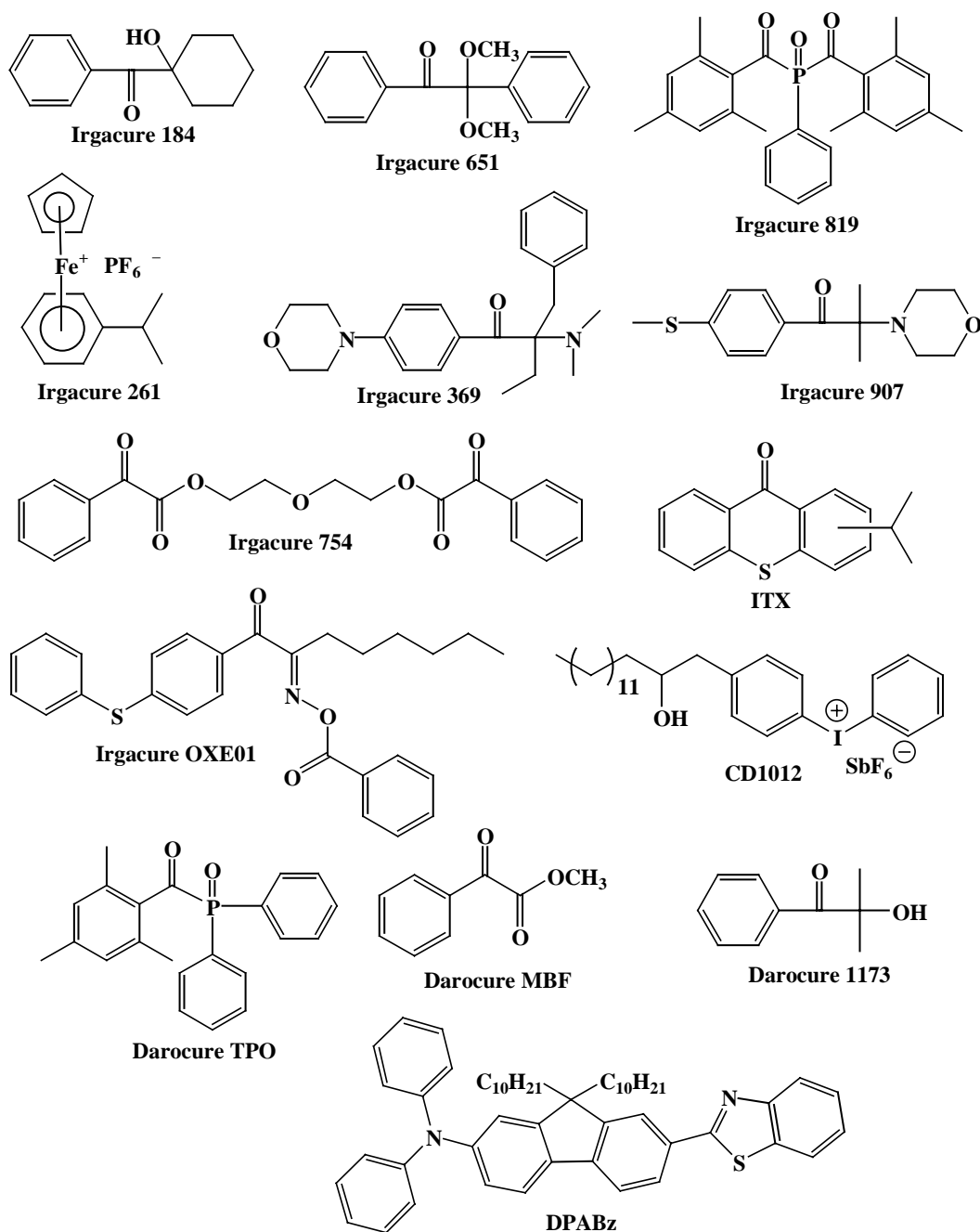
Fig. 1. Structures of the photoinitiators.

in Figs. 1 and 2, respectively. As can be seen, none of the initiators exhibit any linear absorption beyond 500 nm.

Fig. 3 shows experimentally measured non-degenerate 2PA spectra collected for three of the compounds (ITX, Irgacure 369, Irgacure OXE01) using the WLC method. The 2PA cross-sections (symbols) are given in Göppert Mayer units. These cross-sections are plotted versus the sum of the energies of the two photons involved in the non-degenerate process (this energy has been converted to wavelength as well for a reference). The lines are representative of the lin-

ear absorption spectra of the corresponding photoinitiators. The non-linear spectra are nearly coinciding with the linear spectra for each of the compounds shown and this coincidence is true for all the compounds investigated in this study. The Z-scan technique was then used to measure the degenerate 2PA cross-section for each of the compounds at a wavelength twice that at which the maximum of the linear absorption spectrum occurs. This was a great benefit since measuring the full-degenerate 2PA spectrum via Z-scan can be quite time consuming. For cases where the non-degenerate
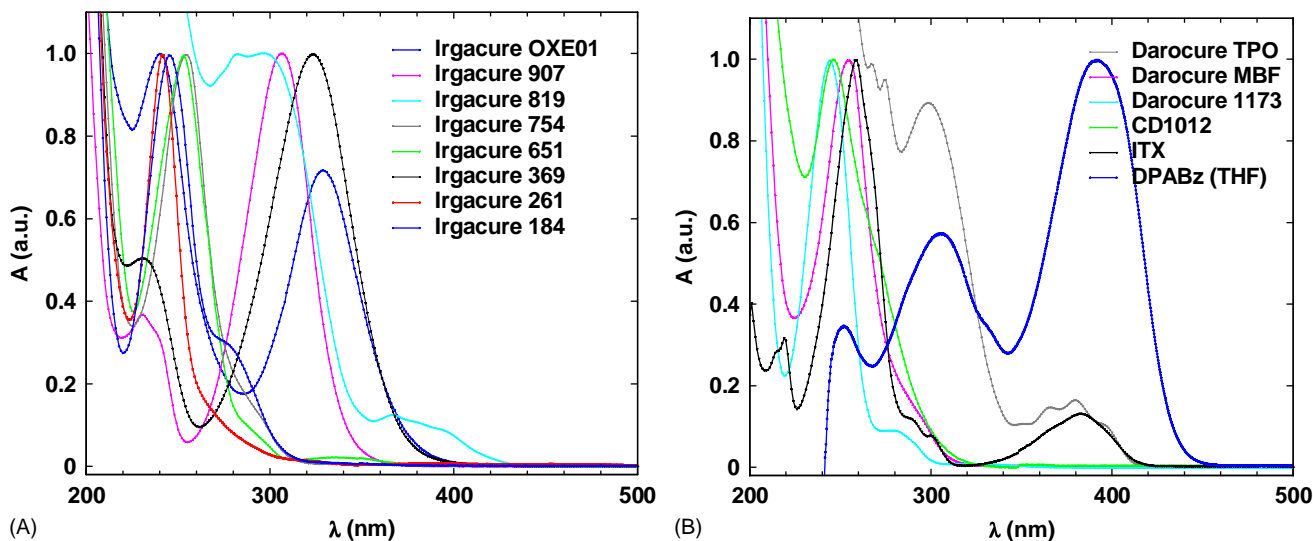
Fig. 2. (A) Normalized UV-visible absorption spectra of Irgacure series photoinitiators in MeOH. (B) Normalized UV-visible absorption spectra of several Darocure, CD1012, and ITX initiators in MeOH. DPABz shown is in THF.

2PA spectra could not be collected (and hence determining the location of the peak of the 2PA spectrum was not possible), measurements in the Z-scan geometry were performed at twice the wavelength of the maximum of the linear absorption spectrum as well as at wavelengths slightly longer and shorter to determine if the measured 2PA cross-section was indeed a maximum. This turned out to be accurate in every case. The full results of the non-linear characterization of the photoinitiators are summarized in Table 1. The first column denotes the peak wavelength (nm) of the linear absorption for each compound. The next two columns reflect the Z-scan results. $\lambda_{meas}^{(2)}$ is given by half the wavelength (nm) of the excitation light and δ_{meas} is the measured absorption cross-section in GM units. The WLC data is presented in the final two columns. $\lambda_{max}^{(2)}$ is the sum of the energies

of the two photons involved in the WLC process expressed in wavelength (nm), i.e. $c/(\nu_1 + \nu_2)$. δ_{max} is the peak 2PA cross-section measured by this method.

Although the WLC method is a rapid characterization technique, it is less sensitive than the Z-scan method. In the case of the Z-scan technique, just four of the compounds were not measurable, but seven had cross-sections too small to be measured by the WLC method. For the cases where the non-linear signal is below the measurable threshold, we have indicated an upper limit to the possible cross-section (e.g. <20 GM). The error bars associated with the measured cross-sections for both methods range from 15 to 20%. Taking into account these error bars, as well as the lower limits imposed on some of the compounds, we consider the agreement between the two techniques for most of the compounds
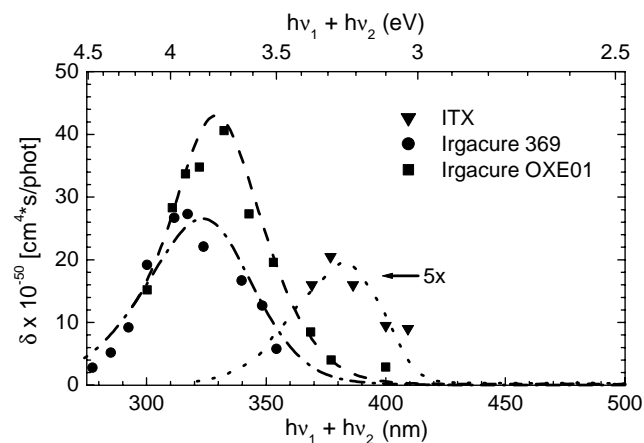

Fig. 3. 2PA spectra via the WLC method. ITX spectrum has been enlarged (5×) for ease of viewing. Lines indicate UV-visible linear absorption spectra: ITX (dot), Irgacure 369 (dash-dot), and Irgacure OXE01 (dash).

Table 1
Peak 2PA cross-sections for photoinitiators using Z-scan and WLC methods

| Compound	λ_{max}	Z-scan		WLC-2PA	
		$\lambda_{max}^{(2)}$	δ_{meas}	$\lambda_{max}^{(2)}$	δ_{meas}
Irgacure 184	246	265	23	250	<20
Irgacure 261	242	265	<20	250	<20
Irgacure 369	324	335	7	318	27
Irgacure 651	254	265	28	250	<20
Irgacure754	253	265	21	250	10
Irgacure 819	295	300	<4	300	<5
Irgacure 907	306	300	4	300	<5
Irgacure OXE01	328	330	31	330	38
Darocure TPO	299	300	<4	300	<5
Darocure MBF	255	265	27	250	<20
Darocure 1173	244	265	<20	250	<20
CD1012	247	265	16	273	14
ITX	382	380	5	377	4
DPABz	390	390	100 (THF)	388	120 (THF)
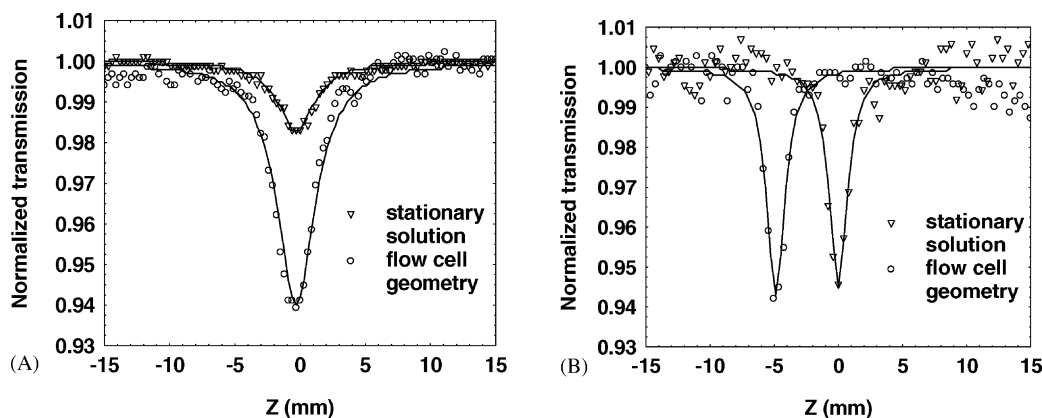
Fig. 4. 2PA results via the Z-scan method for stationary cell and flow cell geometries. (A) Irgacure OXE01. (B) Irgacure 369. Note: The two curves in (B) have been displaced by 5 mm purely for ease of viewing.

to be good, with the largest difference occurring for Irgacure 369.

These compounds undergo photolysis reactions upon photoexcitation and therefore the possibility of photodegradation of the compounds during measurements must be considered. Since 2PA is involved in the photoinitiating process under investigation, there is a concern that during the measurement of the absorption cross-section the molecules could photodegrade which would in turn affect the observed cross-section. Because 2PA increases with increasing irradiance, the possibility of photodegradation should be more prevalent in the Z-scan technique where higher irradiances are used ($50–400\,GW/cm^2$) compared to those used in the WLC method ($<50\,GW/cm^2$). Furthermore, in the WLC method there is no degenerate 2PA of the strong pump beam, only simultaneous non-degenerate 2PA of the pump and probe beams. Since the monitored change in transmittance is of the *weak* probe beam, this guarantees that the population promoted into the excited state is small. Conversely, the Z-scan technique monitors a transmittance change in a *strong* pump beam, which places a larger population into the excited state. Since the number of electrons promoted into the excited state dictates the amount of possible photoreaction, the Z-scan technique is more invasive than the WLC method. It is important to note that even though the WLC is broadband in nature, it did not possess wavelengths short enough for any significant linear absorption that could have caused photodegradation itself.

To investigate the effect of this potential photodegradation, Z-scan measurements were performed on solutions in an enclosed cuvette as well as in a flow cell (both with 1 mm path length). In the flow cell geometry, the cell volume was approximately, 300 μl and the flow rate was approximately, 1.5 ml/s. Flowing the irradiated sample out of the focal region assured that a fresh volume of solution was measured with nearly every laser pulse. A difference between results

obtained with a stationary versus flowing solution is an indicator of photodegradation. A sampling of these results is presented in Fig. 4, where the symbols represent experimental data and the solid lines are their theoretical fittings [16]. Fig. 4A shows the non-linear signal from the flow cell geometry for Irgacure OXE01 was 3.5 times larger than that of the stationary solution, indicating the possibility that photodegradation can interfere with the measurement of the 2PA cross-section if precautions are not taken to avoid this. This also suggests that Irgacure OXE01 should be an effective photoinitiator since it readily undergoes photolysis upon near-IR two-photon excitation. The flow cell data results are the ones presented in Table 1.

Fig. 4B displays the data for Irgacure 369, with the two curves displaced for ease of viewing. It is apparent here that employing the flow cell geometry does not have a significant effect on the non-linear signal. Therefore, the remaining discrepancy between the WLC data and the Z-scan data for Irgacure 369 must be due to some other effect. It should be noted that, although not previously stated, there are fundamental differences in degenerate and non-degenerate 2PA. In general the magnitude of the non-degenerate 2PA spectrum will be enhanced with respect to the degenerate one. This is due to the fact that the positions of the virtual transitions are different for each process and it is their proximity to the nearest excited state that dictates the magnitude of this enhancement. However, in the experiments carried out by the WLC method, the pump and probe photon energies are not strongly disparate and therefore the resulting non-degenerate spectra should not vary far from the degenerate 2PA results. This is evidenced in the results presented in Table 1. Unfortunately, this still leaves an unexplained discrepancy between the two sets of data for Irgacure 369. This may point to a deleterious effect that occurs within the pulse width of the excitation beam and cannot be compensated for in our flow cell geometry; however, this point is still under contention.

4. Conclusions

We have measured the peak 2PA cross-sections for a number of commercially available photoinitiators using two different methods: Z-scan and the WLC method. The results of the two methods provide good agreement for most of the compounds studied (within experimental error). Furthermore, the cross-sections for compounds CD 1012 and ITX agree well with previously reported values in the literature [3]. Irgacure OXE01 possessed a reasonably high two-photon absorption cross-section and underwent relatively fast photolysis as evidenced by comparing the stationary versus flow cell experiment, making it a particularly promising initiator for near-IR two-photon polymerization and microfabrication. DPABz, prepared in our laboratories, exhibits high 2PA and was found to be useful as a two-photon free-radical photoinitiator. It is expected that the field of two-photon absorbing photopolymerization and microfabrication will benefit from new photoinitiators that exhibit even higher 2PA.

Acknowledgements

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