New Developments in Initiators for Two-Photon Polymerization

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ABSTRACT

Two-photon induced polymerization (TPIP) allows greatly improved spatial resolution relative to traditional one-photon polymerization. The main limiting factors of the technology are the high cost of pulsed lasers, slow writing speeds, and poor reactivity of traditional initiators. We address the third issue through synthesis of a series of benzylidene ketones with both high two-photon absorbance and good initiating efficiency. As a result, sub-micrometer structures are produced both faster and with lower required laser intensity.

INTRODUCTION

TPIP is receiving increased attention as a three-dimensional (3D) fabrication method for different mechanical, electronic and optical micro devices, high-density 3D optical data storage, photonic crystals[1,2], polymer-based optical waveguides on integrated circuit boards[3], high-density 3D optical data storage[4,5], and the like. The sub-micrometer resolution and the versatility in the building process offer new routes for medical applications, such as tailored replacement materials. The near-IR laser source penetrates deeper without damaging tissue like UV. With two photon absorption occurring only within the focal point of the laser it is possible to define structures with feature sizes (~120 nm) below the diffraction limit of light[6].

In the early days of TPIP research, commercially available radical PIs such as Irgacure 369 were investigated and found to be insufficient mainly due to low TPA cross sections (σ_{TPA}).[2] Relatively high concentrations, laser intensities, and long exposure times are needed when structuring with Irgacure 369, often resulting in damage to the polymeric structures. An efficient TPIP process requires active two-photon absorption photoinitiators (TPA PIs), which ensure high writing speeds, a low polymerization threshold and therefore high quality structures. In the last decades, plenty of TPA chromophores with large σ_{TPA} were synthesized but only a limited number of them can be used as efficient TPA PIs.[7-9] The main reason is that the rate of free radical photopolymerization is determined not by TPA alone, but also from the quantum yield of radical generation and the initiating efficiency of the formed radicals.[10]

TPA PIs are usually dipolar or quadrupolar molecules with planar π conjugated bridges connecting electron donor and/or acceptor moieties.[11] In comparison to classical UV-vis PIs, TPA PIs have developed slower and have mainly been limited to academic research. One reason for industrial hesitation has been the complications and expense of synthetic routes to planar quadrupolar molecules. For example, double bonds are commonly introduced into the π systems as bridges to extend the conjugation length. This has often been accomplished by classical Wittig[12] or Horner-Wadsworth-Emmons (HWE) reactions[13] of non-commercial Wittig or HWE salts with corresponding aldehydes under strong alkaline conditions. Products from Wittig and HWE reactions must undergo a further synthetic step to provide the desired isomer.[14] Extra steps mean additional time and resources at the expense of overall product yield. The development of simple and economical synthetic routes to prepare TPA PIs remains an open topic.

Recently, Wu's group synthesized a series of benzylidene cyclopentanone dyes and successfully applied them to initiate TPIP.[15,16] The benzylidene ketone core of these molecules is formed in one step via a classical aldol condensation. Although structure-property relationships were conducted on the terminal donor groups[17] and on the electron bridge length [18], the role of the central ketone on TPA has yet to be systematically studied. We have prepared three benzylidene ketones with different central moieties and investigated their photochemical behaviors in TPIP. For comparison, the highly efficient TPA PI **R1** which is well-known from literature[8] was also tested. Investigation on the photophysical properties of the initiators was conducted via UV-vis absorption and emission as well as z-scan measurements. Quantum chemical calculations were carried out to study the structure-property relationship and the calculated results were compared with the experimental ones. Finally, TPIP structuring tests at different laser intensities and feed rates were performed to evaluate the TPA initiation efficiency of each initiator.

RESULTS AND DISCUSSION

Synthesis

The TPA PIs were synthesized via a classical base-catalyzed aldol condensation reaction between N-substituted benzaldehydes and corresponding ketones (see **Figure 1**), both of which are commercially available and inexpensive.[19] The yields after purification by column chromatography or recrystallization were 79%, 57% and 40% for **M2K**, **B2CPK** and **M2CMK**, respectively. Unlike classical Wittig or HWE reactions, which usually generate cis- and trans- isomer mixtures, exclusively all-trans products were obtained in the aldol condensation reactions. The trans-configurations were confirmed by ^{1}H NMR. The proton signals for the CH= group in cycloketone compounds appear at 7.50-7.77 ppm. The chemical shifts of E-isomers are usually higher than 7.2 ppm, while the characteristic peaks for the Z isomers appear at ~6.8 ppm. A coupling constant of 15.72 Hz for double bond protons was found, which is typical for the trans-isomers in the case of **M2K**.
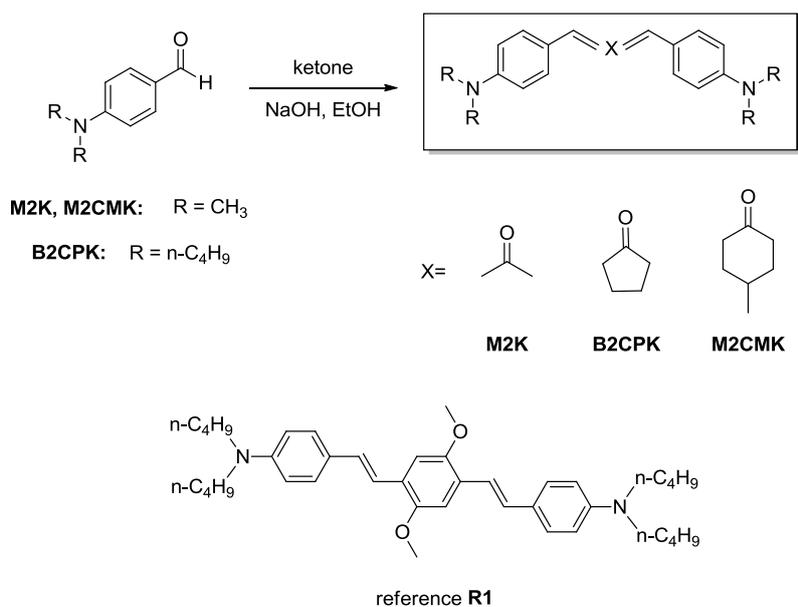
Figure 1. Novel TPA PIs and reference compound

Quantum chemical calculations

To elucidate structure-activity relationships of the novel TPA PIs, quantum chemical calculations at the B3LYP/6-31G (d) level of theory[20] were carried out (shown in **Figure 2**). While good co-planarity of the chromophore's π system is desired for efficient two photon absorption,[11] the optimized structure of reference compound **R1** is not planar. Apparently due to the large NBu$_2$ groups with a strong pyramidality at the N atom (dihedral angle is about 26°), the aromatic rings on both sides are rotated by about 9° relative to the plane of the central ring. The optimized structure of **M2K** has a planar geometry with only a small distortion at the NMe$_2$ groups. **B2CPK** shows a strong deformation at the cylopentane ring, apparently due to the strong distortion induced by the large NBu$_2$ groups. The two aromatic rings are twisted with respect to each other by about 41°. **M2CMK** is not planar due to the cyclohexane ring, however the two aromatic rings are perfectly within the same plane.
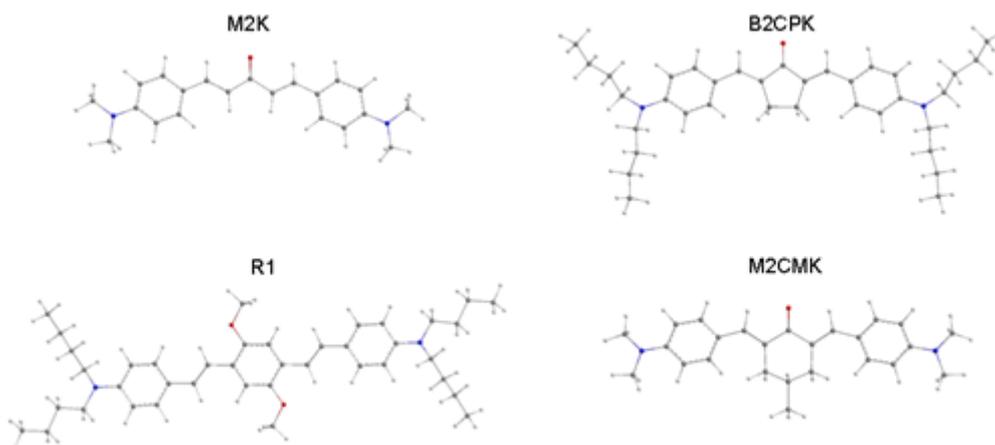
Figure 2. Optimized structures of novel TPA PIs and reference compound

Spectroscopy (UV-Vis and Z-scan analysis)

Important photophysical parameters were measured for the three novel TPA PIs (in dichloromethane) and for **R1** (in acetonitrile) and are presented in **Table 1**. Besides high TPA cross sections, it is favorable for TPA PIs to exhibit low fluorescence quantum yields Φ_f as fluorescence poses an alternative pathway to dissipate the energy of the excited state at the expense of the desired initiation of polymerization.

Table 1. Absorption maxima (λ_{max}), molar extinction coefficients (ε) at λ_{max} and at half the wavelength of the σ_{TPA} measurement (400 nm), fluorescence quantum yields (Φ_f) and two-photon cross sections σ_{TPA} of new TPA PIs and reference compound

Substance	λ_{max} (nm)	ε (10^3 M^{-1} cm^{-1})	ε^{400nm}	Φ_f	σ_{TPA} (GM[a])
M2K	441	47	28	0.15	349
B2CPK	481	78	15	0.20	327
M2CMK	432	51	33	0.0095	191
R1[b]	428	65	44	0.59	318

[a]1 GM = 10^{-50} m^4 s photon^{-1}, reference Rhodamine B has σ_{TPA} of 114 GM (in MeOH) [b]measured in acetonitrile

TPIP microfabrication

Defined woodpile structures (lateral dimension: 50 × 50 µm, 10 µm hatch-distance, 0.7 µm layer-distance, 20 layers) were written into a 1:1 mixture of trimethylolpropane triacrylate (TTA) and ethoxylated (20/3)-trimethylolpropane triacrylate (ETA) by means of TPIP to evaluate the activity of the PIs. The same molar PI concentration of 6.3 × 10^{-6} mol PI/g resin was used, since good results had been previously obtained for such a formulation. The laser intensity was screened in a range of 1-27.8 mW (measured after passing the 100× microscope objective). The different color of the bars and their corresponding classes in **Figure 3** were used to evaluate the TPA initiation efficiency of the initiators. Four classes were employed to indicate the quality of the structures: class A defines excellent structures with fine hatch-lines and class B good structures with thicker hatch-lines or slightly contorted structures, class C has identified shapes but with small mistakes (e.g., holes, exploded regions caused by overexposure) and class D denotes inacceptable results. Generally, broader ideal processing windows (class A and B) and lower laser intensities are desired for high throughput in mass production. Delicate 3D models with high spatial resolution like the dodecahedron depicted in **Figure 3** (85 x 85 x 85 µm^3 in dimensions) can be easily obtained with **M2CMK** in less than 5 minutes writing time.
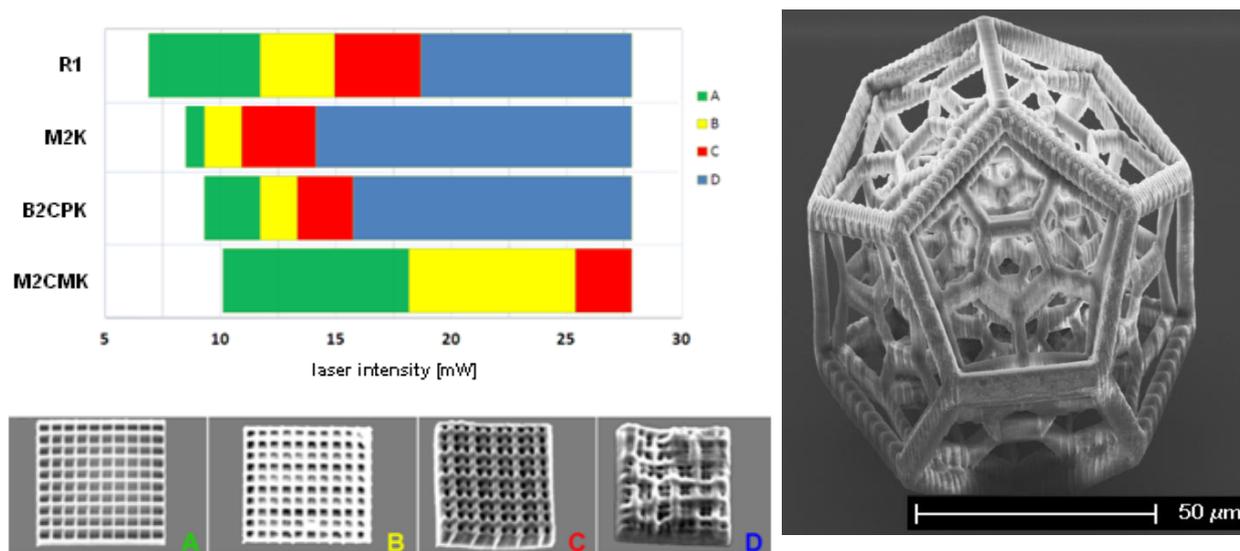
Figure 3. TPIP structuring tests and classification of the structures by the typical quality of their shapes.[19] Intricate free-form structures can be realized with the novel TPA PIs.

CONCLUSIONS

A series of benzylidene ketone-based two-photon initiators containing dialkylamino donor groups and double bonds as conjugation bridges were synthesized via classical Aldol condensation reactions. The systematic evaluation of structure-property relationships via quantum chemical calculations combined with experimental tests confirmed the significant central ring effects on the photophysical and photochemical properties.

Despite the higher co-planarity of **M2K** compared to **B2CPK**, the latter shows a slightly broader ideal processing window, possibly caused by the rigidity of the central ring, which confines the rotation of the double bonds and thus reduces the E/Z-isomerization deactivation. Surprisingly, although **M2CMK** exhibits the smallest σ_{TPA} among the investigated PIs it outperforms both other benzylidene ketone PIs and the reference **R1** in TPIP tests, possessing a much broader ideal processing window. The improved performance likely derives from the much lower fluorescence emission of **M2CMK**. A writing speed as high as 500 mm/s was obtained for microfabrication of complex 3D structures with acrylate-based formulations containing **M2CMK** as photoinitiator. The straightforward synthesis routine combined with high TPA initiation efficiency as well as excellent thermal and one-photon stability of such novel TPA initiators promises great potential for commercialization.

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