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Synthesis and properties of four new two-photon polymerization initiators with expanded conjugated structures

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Synthesis and properties of four new two-photon polymerization initiators with expanded conjugated structures

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Abstract. Four new two-photon polymerization initiators have successfully synthesized with D- π -A- π -D type structure in which the carbazole or phenothiazine moiety acts as a donor, phenylacetylenyl as a conjugate linker and the Fluorenone or thioxanthone as an acceptor. These four compounds exhibited low fluorescence quantum yields (Φ) of **FT-CAA-C6** (1.65%), **FT-PTAA-C6** (0.01%), **TX-CAA-C6** (3.56%) and **TX-PTAA-C6** (0.02%) in dichloromethane. And, the δ_{TPA} values of **FT-PTAA-C6** reached a maximum value of 527 GM. In addition, three-dimensional woodpile microstructure was fabricated via two-photon polymerization using **FT-CAA-C6** as an initiator which possessed potential applications due to simple preparation.

1. Introduction

In the past decade, microfabrication technology by two-photon polymerization (TPP) of photoresist resins has been intensively studied which has emerged as a promising technique for rapid and flexible fabrication of high-resolution three-dimensional (3D) structures [1-5]. Applications for this technology are numerous and include micro-electromechanical systems (MEMS), 3D optical integrated circuits, metamaterials and so on [6-7]. In TPP microfabrication technology, the spatial resolution is dominantly determined by laser power and exposure time, which largely depends on the efficiency of TPP initiators [8-9]. Thus, the crucial factor in TPP materials is photoinitiator which plays an important role in increasing TPP microfabrication lateral resolution. However, the commercial photoresist resins using conventional ultraviolet (UV) active initiators which have low two-photon absorption (TPA) cross-sections (δ_{TPA}). So, high excitation power and long exposure times are necessary to induce polymerization, which often result in burning to the materials. In order to realize the full potential of the two-photon polymerization microfabrication technology, highly active two-photon polymerization initiators (TPPI) with a large δ_{TPA} are desired [10-11].

In general, the molecules with large δ_{TPA} having a general structure of the types D- π -D, A- π -A, D- π -A (A: acceptor, D: donor, and π : conjugating moiety) [12-13]. In order to systematically increase the δ_{TPA} , the design of new materials must deliberate several essential parameters, such as increasing the strength of the donor and acceptor, increasing the planarity of the chromophores, and extending length of the conjugated bridge [14]. Carbazole and phenothiazine are well known donors with electron rich nitrogen or sulfur atoms, which are widely present in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), dye-sensitized solar cells (DSSCs), and polymeric optical fibers (POFs) [15-19]. Fluorenone and thioxanthone are good acceptors with electron-withdraw carbonyl group, which are often present in commonly ultraviolet initiators [20-26]. Herein, we



designed and synthesized four new TPP initiators with D- π -A- π -D type structure which the carbazole or phenothiazine moiety acts as a donor, acetynyl as a conjugate linker and the fluorenone or thioxanthone as an acceptor (Figure 1). Furthermore, we studied their one- and two-photon optical properties, investigated their TPP initiating properties, studied the relationship between initiating efficiency and molecular structure.

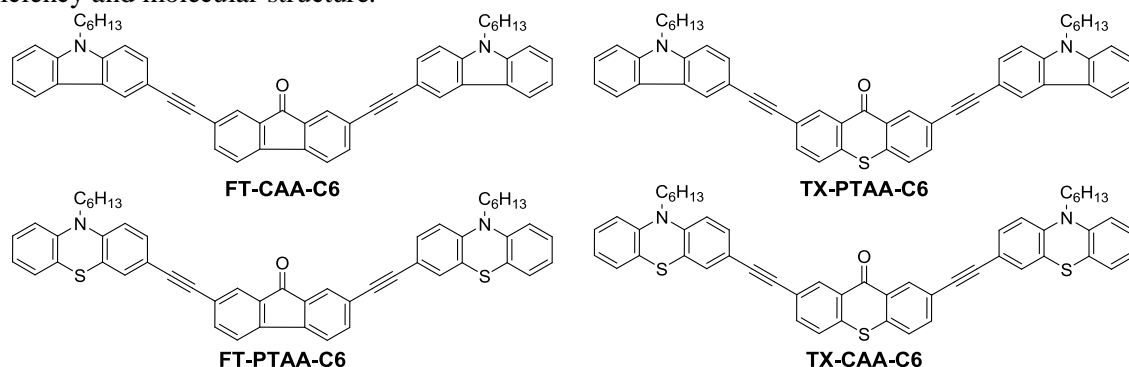


Figure 1. Structures of the four target compounds.

2. Experimental

2.1. Materials

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification.

2.2. Physical measurements

NMR spectra were obtained on a Bruker AV II-400 MHz (¹H NMR at 400 MHz, and ¹³C NMR at 100 MHz). The ¹H NMR chemical shifts were measured relative to CDCl₃ (δ = 7.26 ppm) as the internal reference. The ¹³C NMR chemical shifts were given using CDCl₃ (δ = 77.16 ppm) as the internal standard. UV-Visible spectra were recorded at the concentration of 1×10^{-5} M on a UV 3600 Scanning Spectrophotometer (Shimadzu, Japan). Fluorescence spectra were recorded at the concentrations of 1×10^{-5} M on a F-7000 spectrofluorophotometer (Hitachi, Japan). TPA spectra were obtained by the two-photon-induced excited fluorescence (TPEF) method reported by Xu and Webb [27], TPEF spectra were recorded on a SD2000 spectrometer (Ocean Optical) with the excitation by a mode-locked Ti-sapphire femtosecond laser (Tsunami, Spectra-Physics) for which the oscillating wavelength, pulse width and repetition rate were 780 nm, 80 fs and 82 MHz, respectively. It is assumed that the fluorescence quantum yield after two-photon excitation is the same as that after one-photon excitation. Then TPA cross-sections were obtained by calibration against **Fluorescein** in aqueous NaOH solution (pH = 11) for the femtosecond measurements [9]. The Two-photon polymerization was finished by nanoscribe GT (Germany) with 780 nm laser wavelength, 200 fs lasing source, and 120mW average power.

2.3. Synthesis

The four target molecules were synthesized in several steps which include Sonogashira coupling reactions from sample materials. General procedure for the synthesis of the four target molecules: A flame-dried sealable tube with a magnetic stir bar was charged with CuI (19.0 mg, 0.1 mmol), PdCl₂(PPh₃)₂ (35.1 mg, 0.05 mmol), PPh₃ (26.2 mg, 0.1 mol), bromo-substituted ketone (0.5 mmol), terminal alkyne (1.5 mmol), and triethyl amine (10.0 mL), and DMF (5.0 mL) under an Ar atmosphere. The tube was sealed and the reaction mixture was stirred at 85 °C for 8 h. After being cooled to ambient temperature, the reaction solution was diluted with 100 mL of ethyl acetate and washed with brine (100 mL*3). The organic layer were dried over MgSO₄, concentrated and purified by column

chromatography on silica gel to provide the desired product. The structure of the products were identified by ^1H NMR and ^{13}C NMR.

2,7-Bis((9-hexyl-9H-carbazol-3-yl)ethynyl)-9H-fluoren-9-one (**FT-CAA-C6**), dark red solid, 66% yield. ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 0.87 (t, $J = 7.2$ Hz, 6H), 1.26-1.41 (m, 12H), 1.83-1.91 (m, 4H), 4.29 (t, $J = 7.2$ Hz, 4H), 7.25-7.29 (m, 4H), 7.36-7.42 (m, 4H), 7.46-7.52 (m, 4H), 7.64 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 2H), 7.67 (dd, $J = 8.4$ Hz, $J = 1.6$ Hz, 2H), 7.83 (s, 2H), 8.11 (d, $J = 7.6$ Hz, 2H), 8.30 (d, $J = 1.2$ Hz, 2H); ^{13}C NMR (400 MHz, CDCl_3 , δ (ppm)): 14.2, 22.7, 27.1, 29.1, 31.7, 43.4, 87.2, 93.3, 108.9, 109.1, 112.7, 119.5, 120.6, 120.7, 122.5, 123.0, 124.3, 125.1, 126.3, 127.3, 129.4, 134.6, 137.6, 140.4, 140.9, 142.9, 192.8.

2,7-bis((10-hexyl-10H-phenothiazin-3-yl)ethynyl)-9H-fluoren-9-one (**FT-PTAA-C6**), yellow solid, 54% yield. ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 0.85-0.89 (m, 6H), 1.28-1.33 (m, 8H), 1.39-1.44 (m, 4H), 1.75-1.82 (m, 4H), 3.82 (t, $J = 7.2$ Hz, 4H), 6.78 (d, $J = 8.4$ Hz, 2H), 6.84 (dd, $J = 8.0$ Hz, $J = 1.2$ Hz, 2H), 6.92 (td, $J = 7.2$ Hz, $J = 1.2$ Hz, 2H), 7.10-7.16 (m, 4H), 7.25-7.26 (m, 2H), 7.29 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 2H), 7.45 (dd, $J = 8.0$ Hz, $J = 0.8$ Hz, 2H), 7.58 (dd, $J = 7.6$ Hz, $J = 1.2$ Hz, 2H), 7.74 (dd, $J = 1.2$ Hz, $J = 0.8$ Hz, 2H); ^{13}C NMR (400 MHz, CDCl_3 , δ (ppm)): 14.1, 22.7, 26.7, 26.9, 31.6, 47.8, 88.7, 91.2, 115.2, 115.6, 116.5, 120.6, 122.9, 124.2, 124.8, 124.9, 127.3, 127.5, 127.6, 130.3, 131.0, 134.6, 137.7, 143.1, 144.6, 145.8, 192.5.

2,7-bis((9-hexyl-9H-carbazol-3-yl)ethynyl)-9H-thioxanthen-9-one (**TX-CAA-C6**), yellow solid, 49% yield. ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 0.88 (t, $J = 7.2$ Hz, 6H), 1.26-1.41 (m, 12H), 1.83-1.91 (m, 4H), 4.29 (t, $J = 7.2$ Hz, 4H), 7.26-7.30 (m, 4H), 7.37-7.42 (m, 4H), 7.48-7.53 (m, 4H), 7.66 (dd, $J = 8.4$ Hz, $J = 1.2$ Hz, 2H), 7.57 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 2H), 8.12 (d, $J = 7.6$ Hz, 2H), 8.32 (d, $J = 1.2$ Hz, 2H), 8.80 (d, $J = 2.0$ Hz, 2H); ^{13}C NMR (400 MHz, CDCl_3 , δ (ppm)): 14.2, 22.7, 27.1, 29.1, 31.7, 43.4, 86.7, 92.8, 108.9, 109.1, 112.8, 119.5, 120.7, 122.55, 122.63, 123.0, 124.3, 126.2, 126.3, 129.1, 129.5, 132.8, 134.7, 136.1, 140.4, 140.9, 178.8.

2,7-bis((10-hexyl-10H-phenothiazin-3-yl)ethynyl)-9H-thioxanthen-9-one (**TX-PTAA-C6**), yellow solid, 51% yield. ^1H NMR (400 MHz, CDCl_3 , δ (ppm)): 0.86-0.90 (m, 6H), 1.28-1.33 (m, 8H), 1.40-1.47 (m, 4H), 1.77-1.84 (m, 4H), 3.84 (t, $J = 7.2$ Hz, 4H), 6.80 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.0$ Hz, 2H), 7.11-7.18 (m, 4H), 7.28 (d, $J = 2.0$ Hz, 2H), 7.32 (dd, $J = 8.4$ Hz, $J = 2.0$ Hz, 2H), 7.49-7.51 (m, 2H), 7.65 (dd, $J = 8.0$ Hz, $J = 1.6$ Hz, 2H), 8.698-8.702 (m, 2H); ^{13}C NMR (400 MHz, CDCl_3 , δ (ppm)): 14.2, 22.7, 26.7, 26.9, 31.6, 47.8, 88.2, 90.7, 115.2, 115.6, 116.5, 122.2, 122.9, 124.2, 124.9, 126.3, 127.5, 127.6, 129.1, 130.3, 131.1, 132.9, 134.7, 136.4, 144.7, 145.8, 178.7.

3. Results and discussion

3.1. Photophysical properties

The one-photon absorption and fluorescence spectra were measured in CH_2Cl_2 ($c = 1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$). The normalized one-photon absorption and fluorescence spectra for the four compounds are presented in Figure 2, these four compounds showed very similar absorption and emission spectra. As shown in Figure 2a, there was no obvious one-photon absorption in the spectral range of 550-800 nm for the four compounds, which indicate that there were no energy levels corresponding to an electron transition in this spectral range. And, the absorption spectrum of each compound exhibits strong absorption below 400 nm. If wavelength of exciting laser appeared in this range, it should be attributed to multi-photon absorption mechanism. From Figure 2b, one can see that under identical experimental conditions, the one-photon excited fluorescence (SPEF) spectra showed a similar trend with the linear absorption spectra. The spectra exhibit a large red-shifted with changing donor group (D). The red shift of **FT-CAA-C6** is obviously larger than others, the emission maximum of **FT-CAA-C6** is 632 nm longer than that of **FT-PTAA-C6** (525 nm), **TX-CAA-C6** (523 nm) and **TX-PTAA-C6** (505 nm).

The photophysical properties for the four compounds were summarized in Table 1. These four compounds exhibited low fluorescence quantum yields (Φ), which might contribute to improvement of non-irradiative decay and higher initiating efficiency.

TPA cross-sections (δ_{TPA}) were measured to understand their TPA behaviour using the two-photon fluorescence method and the normalized TPA spectra of **FT-CAA-C6** and **TX-CAA-C6** are presented in Figure 3. However, the two-photon-excited fluorescence spectra of **FT-PTAA-C6** and **TX-PTAA-C6** were not obtained, because of the low fluorescence quantum yields (Φ) of **FT-PTAA-C6** (0.01%) and **TX-PTAA-C6** (0.02%).

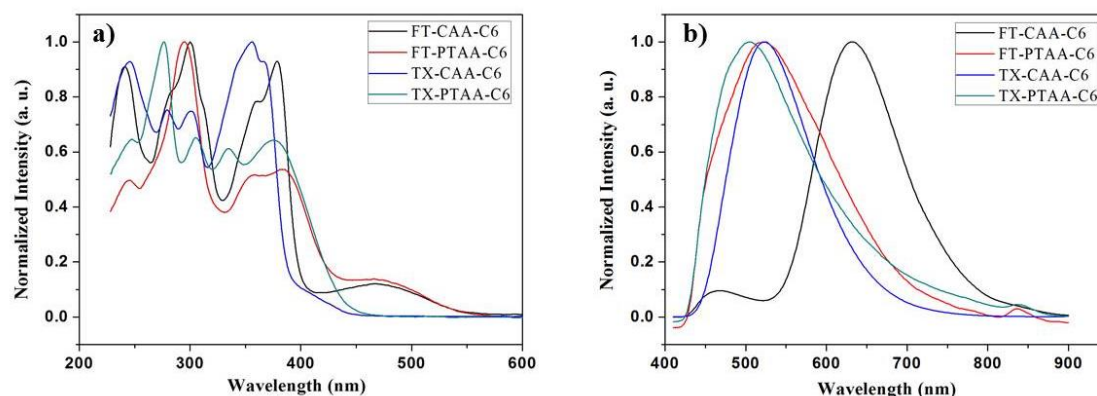


Figure 2. Normalized UV-Vis and fluorescence spectra of **FT-CAA-C6** (black line), **FT-PTAA-C6** (red line), **TX-CAA-C6** (blue line) and **TX-PTAA-C6** (green line) in dichloromethane.

Table 1. Photophysical data of four target molecules in dichloromethane.

Molecule	λ_{\max}^a	$\lambda_{\max}^{\text{SPEF},b}$	Φ^c	$\lambda_{\max}^{\text{TPEF},d}$	$\delta_{\max}^{\text{TPA},e}/\text{GM}$
FT-CAA-C6	300	632	1.65%	617	527
FT-PTAA-C6	295	525	0.01%	-	-
TX-CAA-C6	356	523	3.56%	511	72
TX-PTAA-C6	277	505	0.02%	-	-

^a λ_{\max} of the absorption spectra in nm.

^b λ_{\max} of the one-photon fluorescence spectra in nm.

^c Fluorescence quantum yield.

^d λ_{\max} of the two-photon fluorescence spectra in nm.

^e The maximum of two-photon absorption cross-section. 1 GM = $10^{-50} \text{ cm}^4 \text{ s photon}^{-1}$.

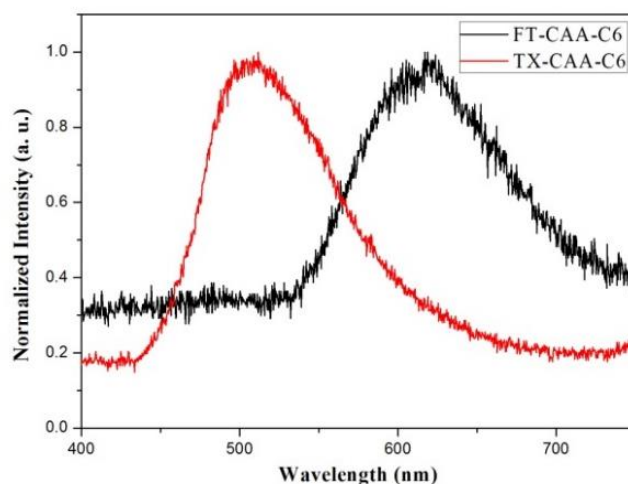


Figure 3. Normalized two-photon-excited fluorescence spectra of **FT-CAA-C6** (black line) and **TX-CAA-C6** (red line) in dichloromethane.

The Figure 4 shows the linear squared dependence of $\text{Log}I_F$ on $\text{Log}I_{in}$ of **Fluorescein**, **FT-CAA-C6** and **TX-CAA-C6** versus excitation wavelengths of 780 nm. The slope values of Figure 4a-c were near by 2, which meant two-photon absorption had occurred. The maximum of δ_{TPA} values of **FT-CAA-C6** (527 GM at 810 nm) and **TX-CAA-C6** (72 GM at 750nm) are also listed in Table 1. The wavelength range 780–820 nm laser light is often used for two-photon microfabrication. Therefore, **FT-CAA-C6** should be promising candidates as photoinitiators.

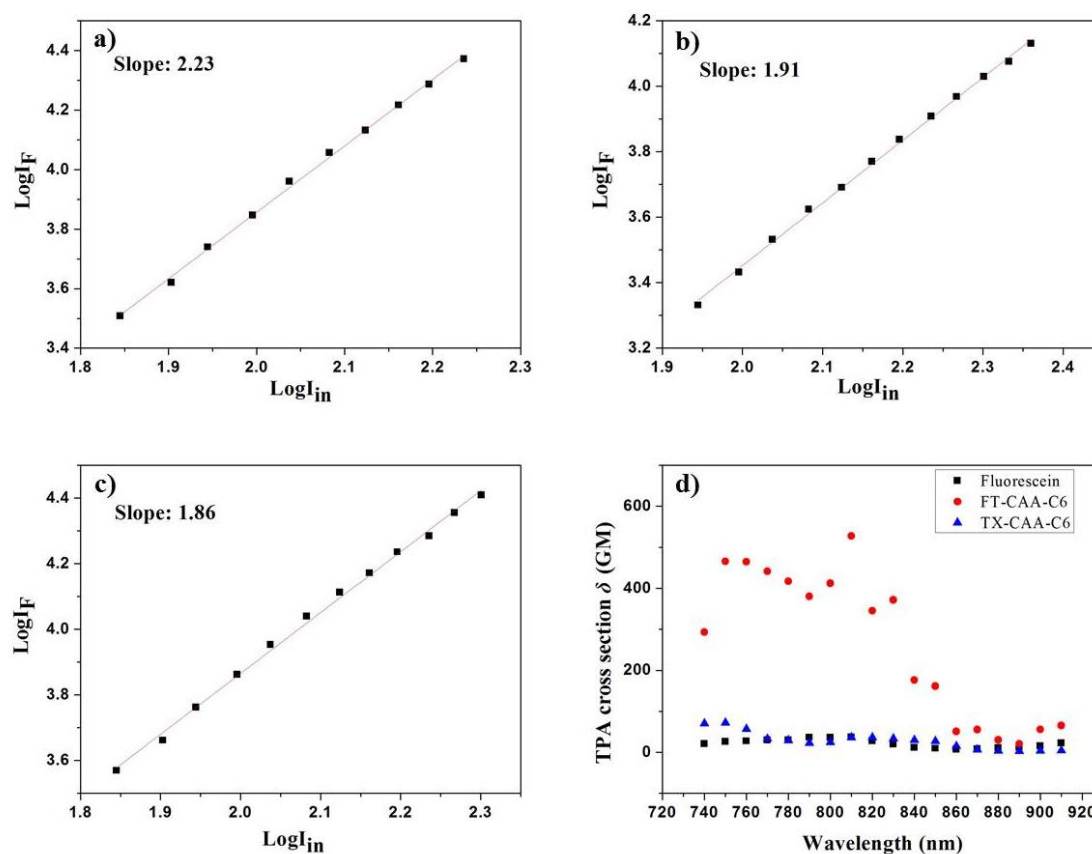


Figure 4. The linear squared dependence of $\text{Log}I_F$ on $\text{Log}I_{in}$ of **a) Fluorescein**, **b) FT-CAA-C6** and **c) TX-CAA-C6** versus excitation wavelengths of 780 nm. **d)** TPA cross-sections of **Fluorescein** (black point), **FT-CAA-C6** (red point) and **TX-CAA-C6** (blue point) in range 740–910 nm. The solvent is dichloromethane.

3.2. Two-photon polymerization

The Two-photon polymerization was finished by nanoscribe GT (Germany) with 780 nm laser wavelength, 200 fs lasing source, and 120mW average power. Three-dimensional woodpile microstructures were fabricated with negative resins system, which contained oligomers (trimethylolpropane triacrylate and trimethylolpropane ethoxylate triacrylate, 1/1, w/w), **FT-CAA-C6** ($c = 10 \mu\text{mol g}^{-1}$) as an initiator and a little N,N-dimethylacetamide (DMAc, increasing the compatibility). The laser was tightly focused via an oil immersion objective lens ($100 \times \text{NA} = 1.4$). The scan speed was $100 \mu\text{m s}^{-1}$. The polymerization results were observed with a scanning electron microscope (zeiss, Germany). It shows a $20 \mu\text{m} \times 20 \mu\text{m}$ polymerization region with a ten layer stereostructure (Figure 5).

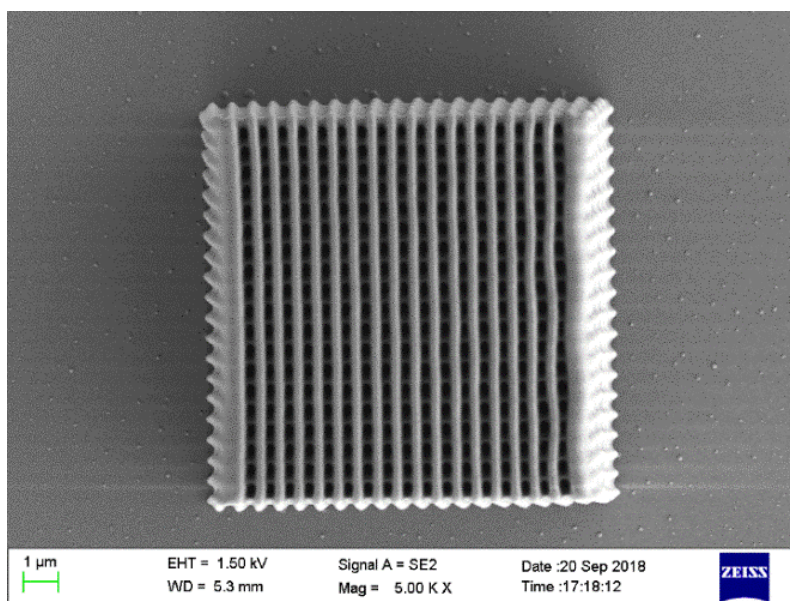


Figure 5. SEM image of the woodpile fabricated via TPP using **FT-CAA-C6** as an initiator.

4. Conclusions

In conclusion, we have successfully synthesized four new two-photon polymerization initiators with D- π -A- π -D type structure which the carbazole or phenothiazine moiety acts as a donor, phenylacetylenyl as a conjugate linker and the Fluorenone or thioxanthone as an acceptor. The δ_{TPA} values reach a maximum value of 527 GM for **FT-PTAA-C6**. In addition, **FT-PTAA-C6** can be used for two-photon polymerization and possess potential applications due to simple preparation.

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