



## A water-soluble two-photon photopolymerization initiation system: Methylated- $\beta$ -cyclodextrin complex of xanthene dye/aryliodonium salt

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### ABSTRACT

An effective two-photon photopolymerization in an aqueous environment was done using a new water-soluble two-photon photopolymerization (TPP) initiation system. This system comprised a photosensitizer dye and the photoinitiator 4,4'-dimethyl diphenyliodonium hexafluorophosphate (DMDPI) encapsulated by methylated- $\beta$ -cyclodextrin (Me- $\beta$ -CD). Photochemical properties of the complex were studied in film. We proved that the complex can be used as an effective TPP photoinitiator for two-photon photopolymerization in an aqueous system. Three-dimensional microstructure was successfully fabricated by TPP.

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### 1. Introduction

In recent years, two-photon absorption (TPA) has shown particular promise in applications for three-dimensional (3D) microfabrication [1], high-density optical storage [2,3], biological imaging [4,5], and photodynamic therapy [6]. Many efficient two-photon absorbing compounds based on molecules having linear or quasi-linear D- $\pi$ -A, D- $\pi$ -A- $\pi$ -D or A- $\pi$ -D- $\pi$ -A structure in which the magnitude of  $\delta$  depends on the degree of intramolecular charge transfer upon excitation have been reported [7–11]. Most of these compounds can be used only in a resin system because of their poor solubility in water. This limitation also prevents their use in biological applications. Solving this limitation is very critical for two-photon technique applications in various biomaterials [12,13]. Recently, some water-soluble TPA materials were successfully developed in biological imaging [14–16]. Very few articles have focused on water-soluble two-photon polymerization (TPP) [12,13].

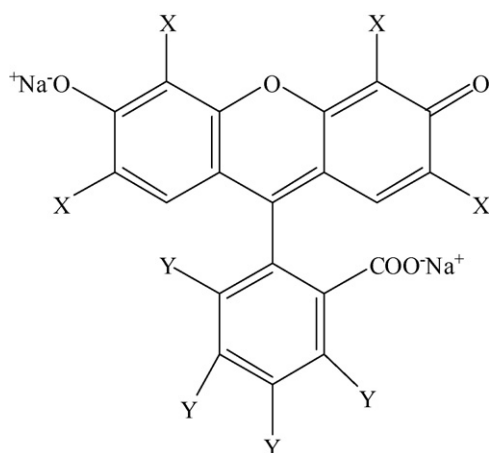
The rate of photopolymerization is mainly influenced by two parameters in TPP: (i) multi-photon absorption cross-section, which provides the probability of multi-photon absorption at a particular frequency and (ii) quantum yield of generated radicals or ions, and the initiation of efficiency of the generated radicals and ions [17]. Designing and synthesizing large cross-section, water-soluble TPA dyes is difficult. Development of a simple method to

ensure TPA dyes with a coinitiator that keeps the higher quantum yield of radical generation and initiation of efficiency would be ideal. Several authors have reported that ion pairing and chemical bonding of the dye and onium salt can eliminate the influence by diffusion. It largely increased the efficiency of the resulting photoinitiators, particularly in highly viscous and rigid polymeric systems [18,19]. Ion-pairing complexation cannot be used in an aqueous system because it will dissociate in the polar medium [20–22]. We recently discovered a promising approach to solve this problem using methylated- $\beta$ -cyclodextrin (Me- $\beta$ -CD) to bind the dye and coinitiator together to form a supramolecular complex [23]. This method has several advantages. Firstly, this photoactive supramolecular complex can be easily obtained using Me- $\beta$ -CD complexation. Secondly, the electron transfer between dye and initiator can occur in the intramolecular complex without the limitation of diffusion rate for common bimolecular reactions. This allows for fast photoinduced electron transfer between dye and initiator within the short lifetime of the dye. Thirdly, the supramolecular complex eliminates the dosage of the coinitiator, thereby significantly reducing material damage and toxicity from residual photoreagents.

Here we report a novel water-soluble two-photon photoinitiation system to carry out an effective two-photon photopolymerization in an aqueous system. The photochemical properties and application for TPP of the supramolecular complex were studied in detail. A very clear microfabrication structure was obtained. This new method is very useful for application of the TPP technique in a water system.

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dye	FL	EO	RB
X	4H	4Br	4Cl
Y	4H	4H	4I

Scheme 1. Chemical structure of FL, EO, RB.

## 2. Experimental

### 2.1. Materials

Me- $\beta$ -CD was obtained from Aldrich Chemical Company. 4,4'-Dimethyl diphenyliodonium hexafluorophosphate (DMDPI) was purchased from TH-UNIS Insight Company Limited. Fluorescein sodium (FL), eosin (EO), rose bengal (RB) were purchased from Beijing Chemical Reagent Company (Beijing, China) (Scheme 1). Acrylamide and bis-acrylamide (AM and bis-AM, Jiangxi Changjiu Biochemical Engineering Co.) were used as received. Hydroxypropyl methyl cellulose (HPMC, 60RT50) was purchased from Repon Chemical Company, and polyvinylpyrrolidone (PVP, Mr, 10,000–70,000) from ShanTou XiLong Chemical Factory (Guang Dong, China).

### 2.2. Photopolymerization

The light source for photolysis was a 400-W Xenon lamp (filter cut off light of  $\lambda < 300$  nm) and the intensity of irradiation was  $4.82 \text{ mW/cm}^2$ . In the photobleaching experiment, the film-forming material was 10% HPMC aqueous solution. Dye/complex A was

added to the solution and poured onto glass substrates. Film thickness was controlled by the scraper and was about  $47 \mu\text{m}$ . Samples were dried in a vacuum oven for 2 h at  $45^\circ\text{C}$ . Photobleaching rate was obtained by the relative change in the maximum optical density of the absorption peak at long wavelength as a function of irradiation time.

### 2.3. Measurements

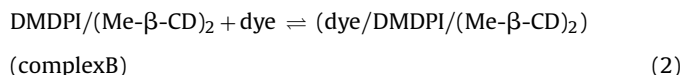
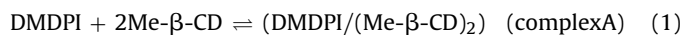
For fabrications of 3D microstructures, we employed a mode-locked Ti-sapphire laser whose oscillating wavelength, pulse width and repetition rate were 780 nm, 80 fs and 82 MHz, respectively. The laser source was tightly focused by a  $100\times$  oil-immersion objective lens with a high numerical aperture ( $\text{NA} = 1.4$ , Olympus). The focal point was focused on the liquid sample, which was placed on a xyz-step motorized stage controlled by a computer. After laser fabrication, unpolymerized pre-polymers were washed out by using ethanol. The two-photon samples consisted of PVP (1 g), AM (1 g), bis-AM (0.1 g) and  $\text{H}_2\text{O}$  (4 g), FL, EO, RB as sensitizer, and complex A as initiator.

Fluorescence measurements were carried out on a Hitachi F-4500 fluorescence spectrophotometer. UV-vis spectra were recorded on a JASCO V-530 instrument.

## 3. Results and discussion

### 3.1. The complex formation

The new two-photon initiating system is a photoactive supramolecular complex (complex B). Formation involves two steps (Eqs. (1) and (2)). Complex B comprises xanthene dye and onium salt DMDPI, in which xanthene dye acts as the photosensitizer and DMDPI as the initiator. Firstly, water-insoluble DMDPI was encapsulated by Me- $\beta$ -CD and became a water-soluble product (Eq. (1)). The obtained complex (complex A) associated with water-soluble xanthene dye via molecular reorganization to form the stable complex B (Eq. (2)). In our previous work, we reported the formation of complex A through encapsulation of Me- $\beta$ -CD [23]. The stoichiometry of host to guest is 2:1; i.e., one molecule of DMDPI associates with two molecules of Me- $\beta$ -CD to form a stable host/guest complex (complex A).



The formation of complex B was examined in aqueous solution by fluorescence spectra. FL is a typical compound of xanthene dyes, and a well-known efficient fluorophore. Interaction between the excited FL dye and complex A can be easily detected by fluorescence

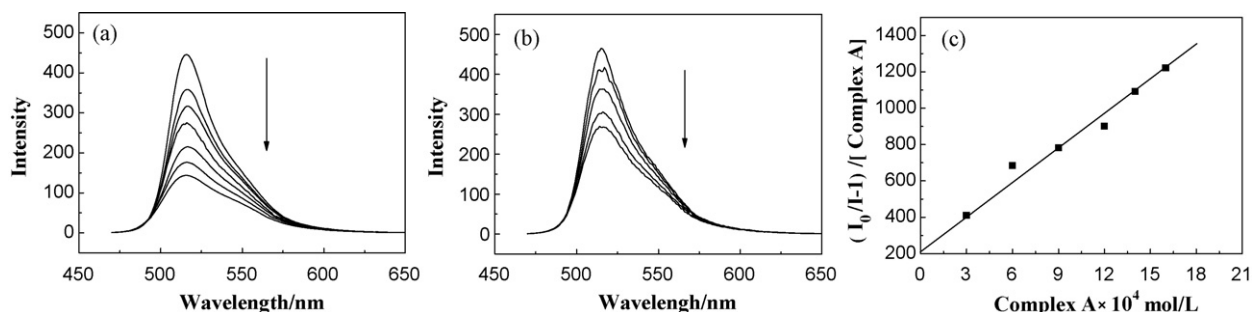


Fig. 1. Steady-state fluorescence spectra of FL dye in aqueous solution and mixed solution ( $\text{CH}_3\text{OH}/\text{H}_2\text{O} = 1:9$ , v/v) at different concentrations of complex A (a) and DMDPI (b). [complex A] = 0, 3, 6, 9, 12, 14,  $16 \times 10^{-4}$  mol/L, [DMDPI] = 0, 3, 6, 9,  $12 \times 10^{-4}$  mol/L. (c) Plot of  $(I_0/I-1)/[\text{Complex A}]$  versus [complex A].

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