



# Synthesis and properties of photochromic spirooxazine with aggregation-induced emission fluorophores polymeric nanoparticles



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## ABSTRACT

We designed and synthesized photochromic fluorescent poly (MMA-co-SPO-co-TPE) nanoparticles with pendant spirooxazine (SPO) dye and tetraphenylethylene (TPE) fluorophores attached to poly (methyl methacrylate) (MMA) backbone by semi-continuous polymerization. The polymerization reactions were accomplished in water with randomly methylated- $\beta$ -cyclodextrin ( $\beta$ -CD) at 80 °C in the presence of potassium peroxydisulfate which can be used as free radical initiator. This new synthetic method leads to uniform and smooth nanoparticles with a narrow particle size distribution. In addition, the poly (MMA-co-SPO-co-TPE) nanoparticles exhibit aggregation induced emission (AIE) properties and excellent photochemical properties because of spirooxazine dyes convert reversibly to merocyanine form upon ultraviolet (UV) irradiation, which active the intramolecular energy transfer pathway and quench the fluorescence of TPE in polymers. Consequently, the fluorescence of the poly (MMA-co-SPO-co-TPE) nanoparticles can be reversibly switched “on” and “off” upon UV and visible light, which may have potential application in biological fluorescent labeling as well as in optical fields like individually light-addressable nanoscale devices.

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## 1. Introduction

Photochromic compounds display a reversible molecular structure transformation, which result in significant absorption spectra change upon the stimulation of ultraviolet (UV) and visible light [1,2]. The special optical property makes them have high potential application in optical data storage, chemical sensors, optical switches, ophthalmic lenses, security documents [3–7]. Among a broad variety of photochromic compounds, spirooxazines have received considerable attention because of their fast response speed and good fatigue resistant [8–10].

Photochromic molecules can be engineered to control the emission of fluorophore-photochrome dyads by energy transfer that caused by reversible photoinduced transformation [11–18]. So

far, a number of photoswitchable fluorescent polymers containing spirooxazine have been reported [19–23] and their development have been extended micrometer/nanometersized level [24]. Photoswitchable fluorescent nanoparticles (PFNs) has been widely studied because of their potential biological application, such as ultrahigh-resolution imaging [25], two photon imaging [26]. Many strategies have been developed to prepare PFNs, such as precipitation, self-assemble method, and emulsion polymerization. However, the self-assembly strategy maybe involves a complicated synthesis and the precipitation strategy often obtained PFNs via doping fluorescence dyes with photochromic molecules or polymer, which will lead to the leakage and aggregation of dyes over time [27–29]. In order to overcome these defects, semi-continuous emulsion polymerization, a facile and simple route was adopted.

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Photoswitchable fluorescent materials are often utilized in their solid states, however, most of the luminophores will lead to aggregation-caused quenching (ACQ). Fortunately, Tang group [30] firstly discovered a new type of fluorescent molecular with Aggregation-induced emission. The AIE effect is opposite to the ACQ effect [31], which makes it more valuable in practical application. In fact, the studies of polymers exhibit photochromic fluorescent properties are rarely reported.

Here, we utilized photochromic molecules spirooxazine (SPO) derivative and the typical AIE molecule tetraphenylethylene (TPE) derivative to prepare a series of polymeric nanoparticles with AIE and photochromic properties via semi-continuous emulsion polymerization. The fluorescence of the polymer nanoparticle can be switched “on” and “off” with UV and visible light.

## 2. Experimental

### 2.1. Materials and instruments

Potassium persulfate (KPS, 99%, Aladdin) was recrystallized from deionized water three times and dried under vacuum. Methyl methacrylate (MMA, 99.5%, Aladdin) was washed five times with 5% sodium hydroxide solution to remove the phenolic inhibitor and then washed with deionized water until the pH was 7. In addition, it was further purified upon distillation under reduced pressure and keep refrigerated for later experiment. Methylated- $\beta$ -cyclodextrin, bromotriphenylethylene, 2-bromoethanol, methacryloylchloride, tetrabutylammonium bromide, tetrakis (triphenylphosphine) palladium (0) were purchased from Aladdin company. 2, 7-dihydroxynaphthalen, 1,3,3-trimethyl-2-methyleneindoline, 4-formylphenylboronic, allyl cyanoacetate were purchased from TCI company. Tetrahydrofuran (THF, A.R) was distilled over CaH<sub>2</sub>. Deionized water was used for all experiments. Other solvents were analytical pure and without any further drying or purification.

Molecular weight of the polymers were obtained by using gel permeation chromatography (GPC). <sup>1</sup>H NMR spectra were obtained by a Bruker Avance 400 NMR spectrometer; UV–Vis spectra were

carried out on Agilent 8453 UV–visible spectroscopy system; Fluorescence spectra were measured by Agilent Cary Eclipse Fluorescence Spectrophotometer. The polymeric nanoparticles diameter distribution and morphology was determined by Zetasizer Nano-ZS MPT and Hitachi S-4800 scanning electron microscope (SEM).

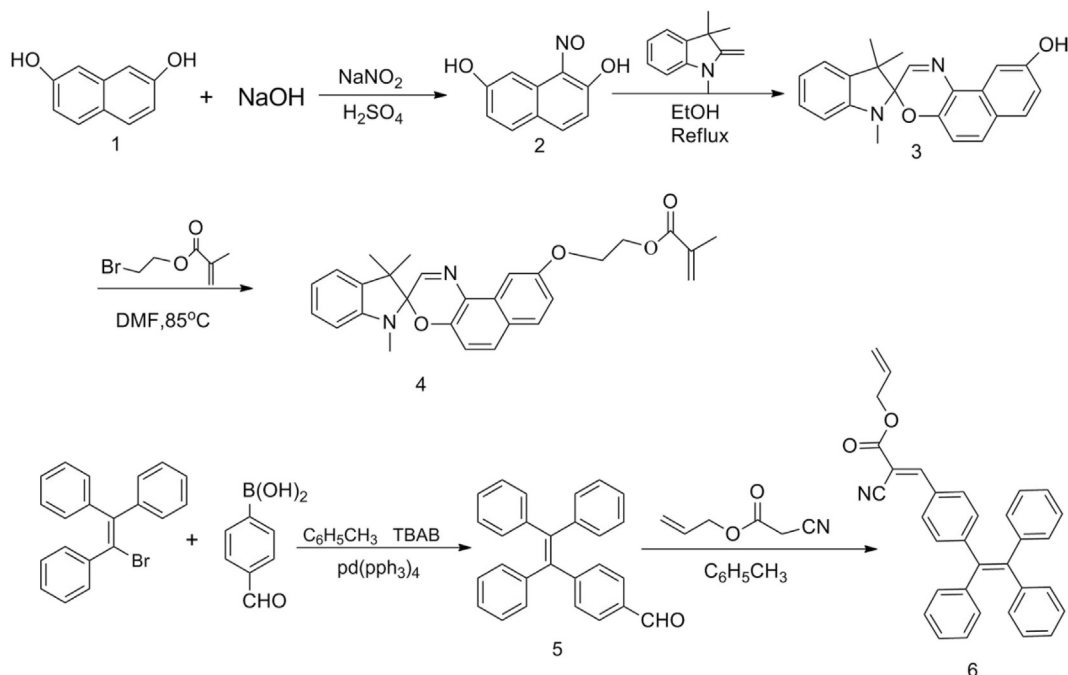
### 2.2. Synthesis of compound 4

Intermediate **3** was prepared according to the literature procedure [32], the preparation method of spirooxazine derivative **4** was follow: adding **3** (1.07 g, 3.1 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.28 g, 9.3 mmol), 2-bromoethyl methacrylate (1.8 g, 9.3 mmol) and KI (0.515 g, 3.1 mmol) in 50 mL DMF, and the mixture was stirred for 48 h at 85 °C. Then dropping them into ice water and filtered. The precipitate was dissolved into ethyl acetate and washed with water three times. The organic phase was dried over anhydrous magnesium sulfate. The purified product was obtained by column chromatography with petroleum ether/ethyl acetate (v/v = 10/1) as eluent, white solid (0.6 g, 42% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (s, 1H), 7.75 (s, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.7, 1H), 7.32–7.21 (m, 1H), 7.11 (t, *J* = 7.1 Hz, 2H), 6.99–6.84 (m, 2H), 6.61 (d, *J* = 7.7 Hz, 1H), 6.22 (s, 1H), 5.63 (s, 1H), 4.63 (t, *J* = 4.7 Hz, 2H), 4.49 (t, *J* = 4.7 Hz, 2H), 2.80 (s, 3H), 2.01 (s, 3H), 1.39 (t, *J* = 3.6 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.39, 157.88, 150.35, 147.62, 144.91, 136.05, 135.88, 132.28, 129.97, 129.58, 128.04, 126.10, 124.81, 122.41, 121.51, 119.86, 117.10, 114.30, 107.15, 100.68, 98.59, 66.00, 63.16, 51.81, 29.66, 25.47, 20.82, 18.38.

### 2.3. Synthesis of compound 6

#### 2.3.1. Synthesis of 4-(1, 2, 2-triphenylvinyl)benzaldehyde 5

Bromotriphenylethylene (3.35 g, 0.01 mol), 4-formylphenylboronic acid (2.25 g, 0.015 mol), 60 mL toluene, anhydrous K<sub>2</sub>CO<sub>3</sub> (4.98 g, 0.036 mol), TBAB (0.3 g, 0.01 mol) were added to 100 mL three-necked, round-bottomed flask in order. The mixture stirred at room temperature under nitrogen atmosphere for 30min. Then, Pd(pph<sub>3</sub>)<sub>4</sub> was added to the flask and the solution was heated to



Scheme 1. Synthetic routes for SPO 4 and TPE 6.

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