



# Reprint of: “AIE luminogen functionalized mesoporous silica nanoparticles as efficient fluorescent sensor for explosives detection in water”<sup>☆</sup>



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## ABSTRACT

The aggregation-induced emission (AIE) luminogen functionalized mesoporous silica nanoparticles (MSNs) were prepared via post-grafting 1,2-bis[4-(bromomethyl)phenyl]-1,2-diphenylethene (TPE-MB) on 3-aminopropyltriethoxysilane modified MSNs. The obtained materials combine the unique properties of the AIE luminogen and porous materials, and their emission wavelength can be changed from 467 to 527 nm by loading different amount of AIE molecules, showing an obvious red shift from blue light to yellow light. Such materials with well dispersibility in water are used as an efficient fluorescent sensor for the detection of explosives, including picric acid (PA), 4-nitrotoluene (4-NT), nitrobenzene (NB) in water. The obtained materials can be recycled by simply washing with proper solvents. The high sensitivity, increased chemical stability and recyclability of the AIE luminogen functionalized mesoporous silica nanoparticles promise that they can be used as an excellent fluorescence probe for future practical applications in explosives detection.

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## 1. Introduction

Considering the high explosively and environmental safety of nitroaromatic explosives, more and more attention has been paid on their selective and sensitive detection in groundwater and seawater [1]. To address this problem, various methods, such as gas chromatography, ion mobility spectrometry, Raman spectroscopy, fluorescence spectroscopy, have been developed in the past several years [2–4]. Especially, regarding the operability and high sensitivity, fluorescence sensing of explosives by harnessing organic dyes demonstrates unique advantages. Whereas suffering from notorious aggregation-caused quenching (ACQ) effect, the aggregation of traditional dyes often quench their light emission in poor solvents or during the formation of film [5], which may limit their further applications in the solid state [6]. In contrast to the ACQ molecules, a series of novel molecules or polymers have been found to luminesce intensively upon molecular aggregation, exhibiting typical aggregation-induced emission (AIE) characteristic [7].

Restriction of intramolecular rotation of multiple phenyl blades has been proposed as the main cause for AIE effect [8–13]. Such materials have been widely used as chemosensors, bioprobes, immunoassay markers, stimuli-responsive materials and solid-state emitters [14]. Particularly, some materials based on AIE luminogens have been applied and shown excellent properties due to their super-amplified performance for explosives. For instance, a novel fluorescent film fabricated by doping aggregates of hexaphenylsilole (HPS) into chitosan, was demonstrated to be highly selective to the presence of picric acid (PA) [15]. However, most of AIE-hybrid materials can only be dispersed in mixed solution of water and organic solvents, so it is highly desirable to develop materials which can be applied in the detection of explosives in water with recyclable property.

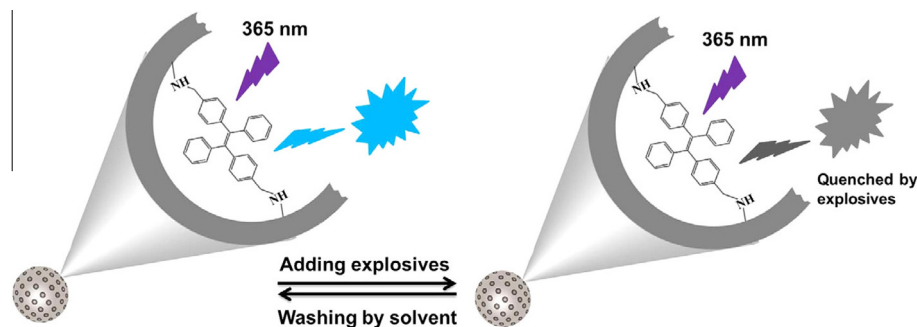
Recently, our group developed a strategy to introduce AIE luminogen tetraphenylethene (TPE) into mesoporous silica SBA-15 via covalent chemical bonding [16]. Such material combines the advantages of the unique properties of AIE luminogen and mesoporous materials, which can enhance mass transport and strengthen interaction with adsorbed explosive molecules. Moreover, since the pore size of the mesoporous materials generally lies in the working distances of photoinduced electron transfer and/or energy transfer, they can be served as potential fluorescent

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**Scheme 1.** The reversible fluorescence quenching mechanism of AIE-luminogen functionalized mesoporous silica nanoparticles for explosives.

chemo-/bio-sensors [17–20]. In the meantime, the additional advantages of the sensors are the increased chemical stability and reversibility, which allows the materials to be recycled. However, the bulk solid materials such as SBA-15 cannot guarantee better dispersibility in water as a result of their large size, which may limit their further applications such as biomedical, chemical detection, etc. As an important type of mesoporous silica, mesoporous silica nanoparticles (MSNs) were successfully synthesized by many groups [21–24]. Due to the excellent dispersibility in solvents and biocompatibility in organism, MSNs with precisely controlled particle sizes ranging from a few to hundreds of nanometers have been widely used in numerous applications such as drug delivery [25], bio-sensing [26] and antireflection (AR) coatings [27].

In this work, we modified mesoporous silica nanoparticles with 1,2-bis[4-(bromomethyl)phenyl]-1,2-diphenylethene (TPE-MB) to form AIE luminogen functionalized materials (FMSNs), and systematically investigated their detection of explosives in water, including picric acid (PA), 4-nitrotoluene (4-NT), nitrobenzene (NB) (Scheme 1). These AIE-luminogen functionalized materials show well dispersibility in water resulted from the nanoscale of MSNs, which guarantees their better stability and sensitivity of explosives detection. We also studied the influence of loading amount of TPE-MB on the photoluminescence (PL) of FMSNs. Their emission wavelength can be adjusted from 467 to 527 nm by loading different amount of AIE molecules, showing an obvious red shift from blue light to yellow light. Importantly, the application of AIE luminogen functionalized MSNs may not be limited to the explosives detection, their tunable emission wavelength and good biocompatibility makes it possible to be applied into organisms for cell-imaging in future potential bioapplications.

## 2. Experimental section

### 2.1. Materials

All chemicals were used as received without further purification. 3-Aminopropyltriethoxysilane (APTES, Sigma–Aldrich), cetyltrimethylammonium bromide (CTAB, Shanghai Wyeth Chemical Co., Ltd.), tetraethoxysilane (TEOS, Beijing Beihua Chemical Co., Ltd.), picric acid (PA, Xilong Chemical Co., Ltd.), 4-nitrotoluene (4-NT, Chengdu Kelong Chemical Co., Ltd.), nitrobenzene (NB, Tianjin Fuchen Chemical Co., Ltd.). Ultrapure deionized (D.I.) water was generated using a Millipore Milli-Q plus system.

### 2.2. Synthesis of monodispersed mesoporous silica nanoparticles

Mesoporous silica nanoparticles (MSNs) were prepared using a base-catalyzed sol–gel method [28]. The molar ratio of CTAB/TEOS/NaOH/H<sub>2</sub>O in the reaction mixture was 1.0:8.16:2.55:4857. In a typical procedure, the aqueous solution of CTAB and NaOH was

stirred at 80 °C for 30 min, followed by the addition of TEOS into the mixture rapidly under stirring, and the solution gradually turned white. After stirred for another 2 h, the solution was cooled to room temperature. The resulting solid product was separated by filtration, washed with plenty of water, ethanol, and then dried in the freezer dryer overnight. The template of MSNs was removed by stirring the material in methanol under reflux overnight. Finally, the product, namely MSNs was dried under vacuum overnight.

### 2.3. Synthesis of AIE functionalized mesoporous silica nanoparticles

1,2-Bis[4-(bromomethyl)phenyl]-1,2-diphenylethene (TPE-MB) was prepared according to the reported method [29]. Mesoporous silica nanoparticles modified with –NH<sub>2</sub> were prepared via post-grafting with APTES [30]. Typically, 500 mg of MSNs was dehydrated under vacuum at 120 °C and then added to a three-neck flask sealed with rubber septums. 1.6 mL of APTES in 5 mL of anhydrous toluene was injected into the system at room temperature. The slurry was refluxed with stirring under N<sub>2</sub> atmosphere for 6 h and filtered, washed with ethanol, and dried at 60 °C for 24 h, the obtained materials were identified as amine-modified MSNs. The amount of NH<sub>2</sub>-groups in amine-modified MSNs was 3.26 mmol/g determined by thermogravimetric analysis (Fig. S1).

AIE-functionalized mesoporous silica nanoparticles were identified as FMSNs. In a typical experimental procedure, 100 mg of amine-modified MSNs and certain amount (0.43 mg for FMSN-1, 0.6 mg for FMSN-2, 1.28 mg for FMSN-3, 2.4 mg for FMSN-4) of TPE-MB were added into 8 mL of DMSO, and the mixture was stirred at 80 °C for 24 h. Filtered and washed with ethanol for several times, the white solid was collected and then dried in the freezer dryer overnight. The residual organic molecules were completely removed after washed with acetone in the Soxhlet extractor, until the characteristic peak of the fluorophore cannot be detected (Fig. S2). The final product was obtained after completely drying at 60 °C.

### 2.4. The detection of explosives with FMSNs

3 mg of as-prepared material FMSNs was well dispersed into 3 mL of water. Certain amount of explosive solution (10<sup>−3</sup> M) was added into the system each time. Meanwhile, the fluorescence emission spectra for samples were recorded with the addition of different amounts of explosives in water solution by spectrofluorometer under UV light illumination (380 nm).

The detection limit ( $C_L$  mol/L) is calculated based on the equation below [31], and  $S_B$  represents the standard deviation of fluorescence intensity in original solution without addition of explosive.  $K_{sv}$  is the quenching constant that is obtained from the fitted exponential equations:

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