



Polymer dots of DASA-functionalized polyethyleneimine: Synthesis, visible light/pH responsiveness, and their applications as chemosensors

Dan Zhong, Ziquan Cao, Bo Wu, Qing Zhang, Guojie Wang*

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, 100083, China

ARTICLE INFO

Article history:

Received 6 March 2017

Received in revised form 12 July 2017

Accepted 14 July 2017

Available online 17 July 2017

Keywords:

Fluorescence
Nanotechnology
Polyethyleneimine
Polymer dot
Sensor

ABSTRACT

Visible light/pH dual-responsive polymer dots (PDs) were facilely prepared from branched polyethyleneimine (PEI) functionalized with donor-acceptor Stenhouse adducts (DASAs). The synthesized polymer dots were characterized by X-ray photoelectron spectroscopy, ^1H NMR spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy (TEM), dynamic light scattering (DLS), UV-vis absorption spectroscopy and fluorescence spectroscopy. The emission peak of the DASA-PEI polymer dots changed as the excitation wavelength varied from 360 nm to 520 nm. The strongest fluorescence emission was located around 522 nm upon 420 nm excitation. Moreover, the DASA-PEI polymer dots exhibited a typical photo-responsive behavior. After visible light irradiation, the triene of DASAs isomerized to the cyclopentenone form. Interestingly, the DASA-PEI polymer dots also responded to acid and alkali and showed a reversible transition between the triene and cyclopentenone isomers. It is demonstrated that the prepared DASA-PEI polymer dots could be applied as a turn-off chemosensor for the rapid and selective detection of Fe^{3+} and Cu^{2+} in aqueous solutions with detection limits of 10.1 nM and 1.3 nM, respectively.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

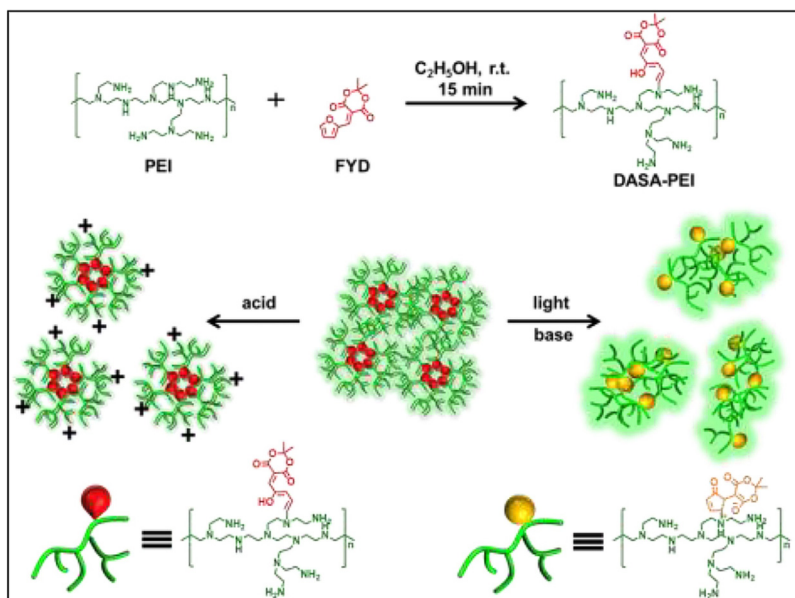
Polymer dots (PDs) are a kind of fluorescent nanoparticles, which possess sub-fluorophores (which are groups such as $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{N}=\text{O}$) instead of typical conjugated fluorophore groups and have a great potential as novel fluorescent materials [1,2]. The strong fluorescence of polymer dots could afford the system as efficient bio-fluorophores for targeted cell imaging [3]. The multifunctional PDs possessing bright and multicolor fluorescence with high drug loading capacity could be used for imaging-guided drug delivery [4]. The polymer dots could be also used as fluorescent chemical sensors to sensitively and selectively detect metal ions [5,6]. Recently, the stimuli-responsive fluorescent materials have attracted ever-increasing attention for their wide applications in the construction of novel detection, imaging, biolabeling, and optoelectronic systems [7]. Of particular relevance to the polymer dots, various research groups have exploited pH, thermal and redox effects on carbon dots [8–13], which have been used in bioimaging [8–12], drug delivery [8,9], and chemosensors [13]. However, to the

best of our knowledge, the dual-responsive polymer dots have not been reported to date.

It is well known that visible light is the most widely available, non-invasive, and environmentally benign external stimulus with the light advantages of spatial and temporal resolution [14–16]. Donor-acceptor Stenhouse adducts (DASAs) are a new class of visible light responsive materials, which can switch from a conjugated, colored, and hydrophobic form to a ring-closed, colorless, and zwitterionic structure upon irradiation with visible light [17–21]. The visible light responsive micelles prepared from DASA-functionalized amphiphilic polymers could display on-demand light-mediated disassembly and cargo release [17]. DASA grafted on amino functionalized polycarbonate surfaces exhibited excellent lithographic performance using visible light, where well-defined patterns could be replicated with high precision and resolution by using suitable masks [19]. A polymeric probe derived from the visible light responsive DASA was designed for the rapid and selective colorimetric detection of nerve agent mimics [21]. As mentioned above, numerous works have been reported concerning polymer dots and visible light responsive DASA-functionalized polymers, however, less attention has been given to the polymer dots based on DASAs. Herein, we report a new kind of DASA-functionalized polymer dots prepared from polyethyleneimine

* Corresponding author.

E-mail address: guojie.wang@mater.ustb.edu.cn (G. Wang).



Scheme 1. Synthetic Scheme for the Preparation of the DASA-PEI and Schematic Illustration of the DASA-PEI Polymer Dots under Visible Light, Acid (pH=6) and Base (pH=8) Stimulation.

(PEI) and 5-(furan-2-ylmethylene)-2, 2-dimethyl-1, 3-dioxane-4, 6-dione (FYD) shown in [Scheme 1](#), which exhibited a characteristic excitation wavelength dependent emission and visible light responsive characteristics. Interestingly, the DASA-PEI polymer dots also showed pH responsiveness. The fluorescence of DASA-PEI PDs could be effectively and selectively quenched by Fe^{3+} and Cu^{2+} in aqueous solutions. We believe that this discovery of the DASA-functionalized polymer dots offers considerable scope for the design of dual-stimuli responsive polymer dots and their applications in detecting Fe^{3+} and Cu^{2+} .

2. Experimental

2.1. Materials

Polyethyleneimine (PEI, Mw = 600), 2-furfural and Meldrum's acid were obtained from Aladdin reagent. Other chemicals were obtained from Beijing Chemical Corp (Beijing, China). Laboratory grade solvents like ethanol and THF were used without any pre-treatment. Deionized water with a conductance below $10^{-6} \text{ S cm}^{-1}$ was applied during the experiments. Stock solutions of metal cations were prepared in distilled water from the respective salts of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CaCl_2 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , MgSO_4 , NaCl , KCl , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

2.2. Synthesis of 5-(furan-2-ylmethylene)-2, 2-dimethyl-1, 3-dioxane-4, 6-dione (FYD)

The compound FYD was synthesized according to the literature.¹⁷ 2, 2-Dimethyl-1, 3-dioxane-4,6-dione (1.51 g, 10.5 mmol) and 2-furaldehyde (960 mg, 10 mmol) were mixed in water (30 mL) and stirred at 75°C for 2 h. After cooling to room temperature, a yellow precipitate was formed. After purification by washing, the compound FYD, a bright yellow powder, was obtained (2.1 g).

2.3. Synthesis of DASA-PEI polymer dots

PEI (0.1 g) and 5-(furan-2-ylmethylene)-2, 2-dimethyl-1, 3-dioxane-4, 6-dione (0.1 g) were dissolved in ethanol (5 mL). Then

the system was stirred at room temperature for 15 min and the color of the mixture changed from yellow to pink. The resultant PDs were precipitated by adding excess THF, which were refined by dissolving in ethanol and precipitating into excess THF 3 times to remove the unreacted FYD. Finally, a pink powder (0.13 g) was obtained after filtering and drying in a vacuum oven for 24 h.

2.4. Determination of fluorescence quantum yield

Quantum yield (QY) measurements were performed according to the established procedure. Quinine sulfate in 0.1 M H_2SO_4 (quantum yield 0.54) was used as a standard [22]. In order to minimize re-absorption effects, the absorbance of the solutions for PDs and quinine sulfate was kept below 0.05 at 360 nm. The QY was calculated using the below equation:

$$\phi_X = \phi_{ST} (I_X / I_{ST}) (A_{ST} / A_{AX}) (\eta_X^2 / \eta_{ST}^2)$$

Where ϕ is the QY, I is the gradient from the plot of integrated fluorescence intensity versus absorbance, and η is the refractive index of the solvent; ST denotes the standard and X denotes the sample.

2.5. Metal ion detection

The metal ion solutions were prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CaCl_2 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , MgSO_4 , NaCl , KCl , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water with a concentration of $500 \mu\text{M}$. For metal ion detection, a calculated amount of Fe^{3+} and Cu^{2+} (0, 10, 20, 30, 50, 100, 200, 300, 400, and $500 \mu\text{M}$) was added to 1 mL aqueous solutions containing $100 \mu\text{g}$ PDs, and allowed to react for 3 min under gently shaking. Then, fluorescence spectra were recorded. All experiments were performed at room temperature.

2.6. Characterizations

^1H NMR spectroscopy was conducted with a Bruker AM 400 spectrometer with $\text{DMSO}-d_6$ as the solvent. The UV-vis spectra of the samples were recorded using a UV-vis spectrometer (JASCO V-570). The fluorescence spectra were recorded on a Hitachi F-4500

Download English Version:

<https://daneshyari.com/en/article/5008689>

Download Persian Version:

<https://daneshyari.com/article/5008689>

[Daneshyari.com](https://daneshyari.com)