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Yellow electrochemiluminescence emission from hydrophilic poly[(9,9-di-(2-ethylhexyl)-9H-fluorene-2,7-vinylene)-*co*-(1-methoxy-4-(2-ethylhe-xyloxy)-2,5-phenylenevinylene)] (PFV) conjugated polymer dots capped with Triton X-100 in aqueous solution

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ABSTRACT

We synthesized new, yellow-light emitting, and hydrophilic poly[(9,9-di-(2-ethylhexyl)-9H-fluorene-2,7-vinylene)-*co*-(1-methoxy-4-(2-ethylhe-xyloxy)-2,5-phenylenevinylene)] conjugated polymer dots capped with nonionic surfactant Triton X-100 (PFV CP-dots@TX), immobilized them on glassy carbon electrodes and studied their electrochemiluminescence (ECL) behaviors and mechanisms in aqueous solutions. The ECL activities of the hydrophilic CP-dots were investigated by applying the glassy carbon working electrode with pulse potential between anodic and cathodic potentials in the absence of coreactant, with sweeping anodic potential in the presence of Tri-*n*-propylamine (TPrA) as the coreactant, and with sweeping cathodic potential in the presence of peroxydisulfate ($S_2O_8^{2-}$) as the coreactant. Experimental results shows that PFV CP-dots@TX have good annihilation ECL activity, anodic ECL activity and cathodic ECL activity. All of the three types of ECL reactions emit yellow light with the maximum wavelength of 573 nm, which is the same as the fluorescence emission spectrum of PFV CP-dots@TX in water. The energies involved in the ECL reactions were analyzed and non-surface state ECL mechanisms were discussed and proposed. The yellow light-emitting, hydrophilic CP-dots are envisioned to be a new type of ECL luminophores that may have promising applications in chemical sensing, biosensing and new optoelectronic devices.

1. Introduction

Recently, so-called conjugated polymer dots (CP-dots), which can be prepared from the well-known conjugated polymers widely applied in optoelectronic devices [1–4], have attracted increasing attention due to their unique advantages such as easy synthesis, small particle size, high brightness, less toxicity and more biocompatibility [5,6]. In addition, the properties of CP-dots can be tuned easily for applications by choosing different conjugated polymers and surface modifications [7,8]. These merits make CP-dots very suitable for applications in chemical sensing, biosensing and bioimaging [9–14].

Electrochemiluminescence (ECL) is an important modern technology in analytical chemistry and biosensing, and has gained more and more applications in various fields such as environmental monitoring and clinic immunoassay [15,16]. Although, in the past decades ECL has made many important progresses both in theoretic study and practical application, it still faces critical challenges in the study and use of ECL luminophores. The reported ECL luminophores includes classic molecular ECL luminophores such as such as luminol and tris(2,2′-bipyridine)ruthenium(II) complexes ($Ru(bpy)_3^{2+}$) [17,18], and ECL nanomaterials such as Cd-based semiconducting nanocrystals (so called quantum dots) [19], carbon-based dots [20], and g-C_3N_4 nanosheets [21]. However, these ECL luminophores suffer from various disadvantages such as high cost (e.g. $(Ru(bpy)_3^{2+}$ derivatives), strong toxicity (i.e. CdS, CdTe, CdSe quantum dots), and single color light emission (e.g. carbon-based dots and g-C_3N_4 nanosheets). The shortage of ECL luminophores, especially hydrophilic ECL luminophores with desired colors, strong light emission, easy synthesis and modification, low cost, and environmental friendliness have limited seriously the extensive applications of ECL. The emerging of CP-dots with above mentioned advantages may open a new window for discovering new types of ECL luminophores with ideal properties.

Recently, ECL of some hydrophobic CP-dots without any coating in organic solvents, such as F8BT CP-dots in acetonitrile [22], and oligothiophene CP-dots in benzene and acetonitrile [23,24], have been investigated. These works show that CP-dots may become new types of ECL luminophores. However, the hydrophobic CP-dots in organic solvents are not applicable for real environmental, biological, and clinic samples which usually dispersed in aqueous solutions. Most recently,

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we found that Triton X-100, a nonionic surfactant, could be used to well cape hydrophobic CP-dots into hydrophilic CP-dots [25]. The obtained hydrophilic ECL luminophore (MEH-PPV CP-dots) exhibited good ECL activities and emitted pink light (590 nm) in aqueous solution, suggesting an efficient way to synthesis hydrophilic CP-dots based ECL luminophore.

It is of considerable research and application interest to find other new hydrophilic CP-dots-based ECL luminophores, especially those hydrophilic CP-dots emitting desired color lights for potential multi-color ECL array sensing in the future. Herein, a yellow ECL emitting CP-dots coated with Triton X-100 (CP-dots@TX) was synthesized from the conjugated polymer called as poly[(9,9-di-(2-ethylhexyl)-9H-fluorene-2,7-vinylene)-*co*-(1-methoxy-4-(2-ethylhe-xyloxy)-2,5-phenylenevinylene)] (or PFV). The synthesized PFV CP-dots@TX exhibited good and versatile ECL activities in aqueous solution (pH 7.0 phosphate solution), including annihilation ECL in the absence of coreactants, anodic ECL and cathodic ECL in the presence of coreactants. The energies available for the ECL emissions were analyzed and non-surface state ECL mechanisms were discussed and proposed. The yellow light-emitting hydrophilic CP-dots are envisioned to be a new type of ECL luminophores that may have promising applications in sensing and new display devices.

2. Experimental section

2.1. Materials

Poly[(9,9-di-(2-ethylhexyl)-9H-fluorene-2,7-vinylene)-*co*-(1-methoxy-4-(2-ethylhe-xyloxy)-2,5-phenylenevinylene)] (PFV, 90:10 mol ratio) was purchased from Sigma-Aldrich. Tri-*n*-propylamine (TPrA) was purchased from Fluka (USA). Triton X-100, tetrahydrofuran (THF, anhydrous), potassium peroxydisulfate ($K_2S_2O_8$), and other reagents used in the experiments were of analytical grade. Phosphate buffer solutions (PBS) of 0.1 M were prepared from mixing concentrated sodium hydroxide solution and phosphoric acid in appropriate ratios. Filter membrane with average pore of 0.22 μm was used in the process of preparing CP-dots. The water used in the experiments was all doubly distilled water.

2.2. Apparatus

UV–vis absorption spectra were characterized by a UV–vis spectrophotometer (TU-1950, Persee). Fluorescence spectra were measured on an F-4600 fluorescence spectrophotometer (Hitachi, Japan). The particle size of the PFV CP-dots was measured by dynamic light-scattering (DLS) technology using a ZetaPALS (Brookhaven Instrument Corporation, USA). ECL and electrochemical measurements were carried out on an EC & ECL analysis system (MPI-E, Remex Electronic Instrument Lt. Co., Xi'an, China) with a three-electrode system consisting of a 3.0 mm diameter glassy carbon (GC) working electrode, a Pt wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode. A set of optical cutoff filters (495, 535, 555, 575, 590,620, 640, and 680 nm) were used to measure ECL spectra by placing them between the light emitting working electrode and the photomultiplier tube of ECL analyzer.

2.3. Preparation of PFV CP-dots@TX

The hydrophilic Triton X-100 capped PFV CP-dots (i.e. PFV CP-dots@TX) were fabricated by using a reprecipitation method mentioned in the literatures with some modification [26]. In a typical procedure, PFV conjugated polymer was dissolved in the tetrahydrofuran (THF) with nitrogen atmosphere protecting for 3 h, then it was filtered to remove any insoluble solid and diluted to get a homogeneous solution with concentration of 100 ppm. 32 μL Triton X-100 was added into 2 mL 50 ppm PFV polymer solution under ultrasonication. After 10 min, the mixed solution was injected into 10 mL ultrapure water under vigorous sonication condition for another 10 min. The resultant PFV CP-dots@TX colloid was partially evaporated under vacuum to remove THF component and then filtrated through a piece of 0.22 μm filter membrane to eliminate large size PFV CP-dots@TX. The prepared hydrophilic PFV CP-dots@TX colloid was stored at 4 °C under darkness condition.

2.4. Preparation of PFV CP-dots@TX-modified working electrode

The GC electrode was polished for 2 min with 50 nm alumina on an electrode polishing machine (Wuhan Gaoss Union Technology Co., Ltd., China) followed by being ultrasonically washed with doubly distilled water twice (each for 1 min) and being dried with a nitrogen gas stream. Then 2 μL of the prepared 5 μg mL^{-1} PFV CP-dots@TX colloid was dropped onto the electrode surface of above treated GC working electrode and dried with anhydrous silica gel in a desiccant at room temperature. The preparation of the PFV CP-dots@TX-modified working electrode at room temperature could be finished within 20 min.

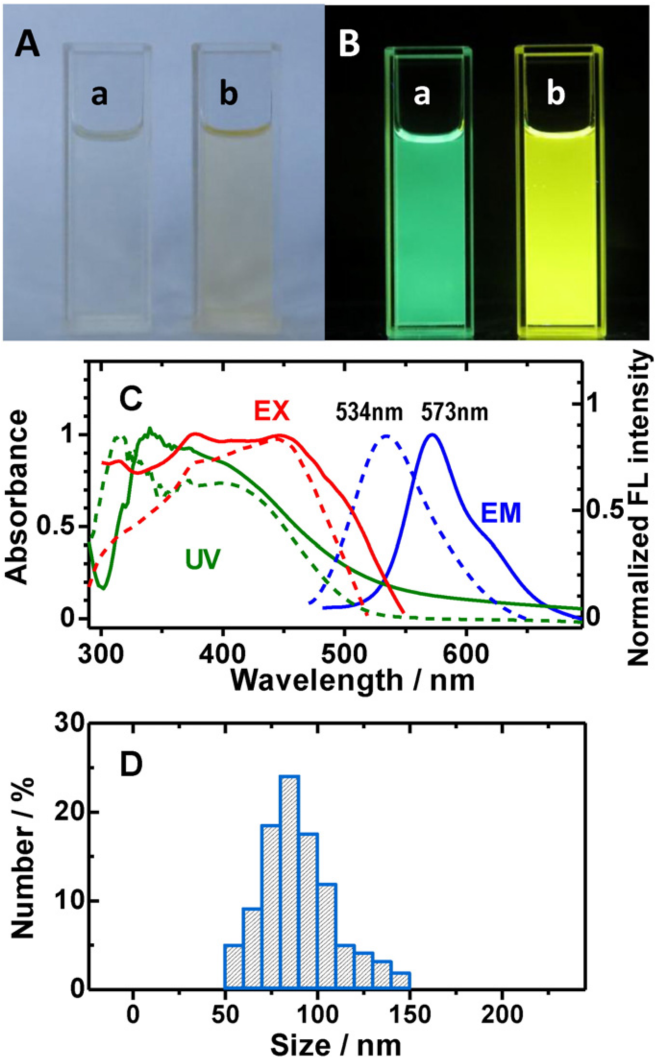

Fig. 1. (A) Photos of PFV polymer in THF (a) and PFV CP-dots (b) in water under white light; (B) photos of PFV polymer in THF (a) and PFV CP-dots in water under 365 nm UV light. (C) UV–vis absorption spectra (green curves), fluorescence emission excitation spectra (red curves) and fluorescence emission spectra (blue curves) of PFV polymer in THF (dash curves) and PFV CP-dots in water under (solid curves); (D) size distribution obtained for CP-dots by DLS.