



# A new type of polymer carbon dots with high quantum yield: From synthesis to investigation on fluorescence mechanism

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## ABSTRACT

Carbon dots (CDs) is an area of intense focus, currently limited to unclear photoluminescence (PL) mechanism. Much effort has been made to clarify the certain PL centers but is still fruitless. Herein, a new type of polymer carbon dots (PCDs) with absolute quantum yield as high as 44.18% was synthesized by hydrothermally crosslinking polyacrylic acid and ethylenediamine. Through carefully comparing and analysing, the PL centers were supposed to be -N=O and -C=O (mainly amide and/or its derived structures) rather than large-scale conjugated structure, which was similar to the previously reported sub-fluorophores. Besides, the function of polymer chains was considered to decrease the motion freedoms and provide a solvation effect by crosslinking and wrapping the fluorescence centers, which led to the improved quantum yield and red-shifted emission. The investigation on fluorescence mechanism can provide with a new understanding on crosslink enhanced emission (CEE) effect in non-conjugated fluorescence systems.

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## 1. Introduction

Carbon dots (CDs) [1–10] has obtained continuous attention owing to its prominent characters and wide application prospects since firstly reported [11]. CDs always possesses nano-sized dot structure and fluorescence as their instinct properties. Compared with the conventional fluorescent dyes, the carbon-based fluorescence material owns various advantages, such as facile synthesis, bright emission, low toxicity and good biocompatibility [12,13]. In the last few years, researchers have prepared a wide variety of CDs by exploiting plenty of preparation methods and the original materials, resulting in large differences on the structure, property and fluorescence mechanism. Up to now, the field of CDs has developed greatly but is also facing large challenges, such as the lack of long-wavelength-emission systems [14–16] and confused fluorescence mechanism [17–19]. More and more researchers are looking forward to finding a systematic way to explain the complicated phenomenon and expand the application fields, which may cause further development in the field of CDs.

In addition, fluorescent polymer is another kind of functional

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materials, which can be applied to the chemical and biological sensing [20,21]. Introducing functional fluorophores onto the polymer chain [22] and polymerizing conjugated monomer [23,24] are two common ways to obtain fluorescent polymer. However, many conjugated polymers suffer from low aqueous solubility and high toxicity, which hinder the direct application of biological sensing. Recent researches found that some non-conjugated polymers were instinctively emissive. Among all, poly(amido amine)s were typical models [25–29], which didn't own common fluorophores but still highly emissive in solution. The hyperbranched structure was inferred as an important factor for the emission [30]. Furthermore, other special fluorescence mechanisms of linear non-conjugated fluorescent polymers were gradually uncovered. For example, Song et al. reported linear polymers containing pyrrolidone rings could exhibit strong fluorescence [31]. The fluorophores were considered to be secondary amine oxide and the strong emission was attributed to fluorophores' aggregation-induced emission effect. Zhao et al. synthesized emissive poly[(maleic anhydride)-alt-(vinyl acetate)] and proved that its emission originated from anhydride cluster interacting in a through-space manner [32].

As their cousin, a new type of fluorescent material polymer carbon dots (PCDs) [17,33–36] is becoming a hot topic, which inherits the advantages of both sides. Typically, PCDs is nano-sized

particle possessing abundant polymer structures with low carbonization degree, prepared from the monomers or non-conjugated polymers by condensation, crosslinking, assembling, or slightly carbonization processes. There is a relationship among the mechanisms of PCDs, CDs and non-conjugated fluorescent polymers, which is waiting to be discovered. Our group also put forward our own opinion on the emission origin of PCDs, previously. Zhu et al. investigated the fluorescence from sub-fluorophores in the non-conjugated polymer or PCDs and found that emission could be enhanced by chemical crosslinking or physical immobilization of polymer chains, which was named the crosslink-enhanced emission (CEE) effect [17,33,34]. Based on the background above, we would like to share our new comprehension on the fluorescence mechanism through investigating a new type of PCDs.

In this paper, we synthesized PCDs with high quantum yield via a one-pot hydrothermal treatment of polyacrylic acid (PAA) and ethylenediamine (EDA). The obtained PCDs was confirmed to be crosslinked nanoparticles with low degree of carbonization and remain characters of polymer. The fluorescence source was inferred as the oxidation product of amine during hydrothermal process. Moreover, the PAA chains played a vital role in forming crosslinked polymer structure and wrapping the fluorophores. The decreased motion freedom led to enhanced emission intensity and the new chemical environment led to red-shifted emission from UV region to visible region. The explanation of PCDs' fluorescence mechanism could further refine our CEE effect theory.

## 2. Experimental

### 2.1. Materials

PAA ( $M_w = 3500$  g/mol), EDA and quinine sulfate were purchased from Aladdin Chemical Co. Sulfuric acid ( $H_2SO_4$ , 98%) and hydrochloric acid (HCl, 36–38%) were obtained from Beijing Chemical Reagent Co. Potassium persulfate was purchased from Tianjin Huadong Chemical Reagent Co. All of the chemicals were used without further purification.

### 2.2. The synthesis of PCDs

PAA (72 mg, 1 mmol -COOH) was dissolved in deionized water (10 mL). After that, EDA (140  $\mu$ L) was added and mixed uniformly. Then the solution was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (25 mL) and heated at different temperatures in oven. However, higher temperature didn't lead to obvious promotion of PL intensity but great damage to autoclave. In comprehensive consideration of product's fluorescence intensity and autoclave's heat-resistance temperature, the experiment condition of 200 °C for 8 h was selected for further studies. After the reaction, the reactors were cooled down to room temperature naturally. The obtained transparent buff solution was dialyzed in dialysis bag (500–1000 D) against deionized water for three days, in order to remove the small molecules. Solid PCDs could be obtained from the solution via freeze-drying. (yield ca. 30%).

### 2.3. The synthesis of EDA-H

Ethylenediamine (EDA, 140  $\mu$ L) was added to deionized water (10 mL). Then the solution was transferred to a poly (tetrafluoroethylene) (Teflon)-lined autoclave (25 mL) and heated at 200 °C for 8 h. After the reaction, the reactors were cooled down to room temperature naturally. The colorless and transparent solution was filtered by 0.22  $\mu$ m polyethersulfone membrane to remove large particles. The product was named as EDA-H. In addition, other EDA

hydrothermal products were synthesized by adding potassium persulfate ( $K_2S_2O_8$ , 5, 25 or 200 mg) in solution before heating.

## 2.4. Characterization

High-resolution transmission electron microscopy (HRTEM) was recorded on a JEOL JEM-2100 F by using ultra-thin carbon films as grids. IR spectra were taken on a Nicolet AVATAR 360 FT-IR spectrophotometer. Zeta potential and DLS were performed using a Zetasizer Nano-ZS (Malvern Instruments). NMR spectra were performed with a Bruker AVANCE NMR spectrometer (500 MHz) using  $D_2O$  as the solvent. Thermogravimetric analysis (TGA) was measured on a Mettler Toledo TGA/SDTA851e instrument under  $N_2$  atmosphere from room temperature to 600 °C with a heating rate of 10 °C per minute. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250 spectrometer with a mono X-ray source with Al  $K_{\alpha}$  excitation (1486.6 eV). UV-vis absorption spectra were obtained using a 3100 UV-vis spectrophotometer (Shimadzu). Static fluorescence spectra were performed on a RF-5301 PC spectrophotometer (Shimadzu). Fluorescence lifetime (with TCSPC technology) and emission spectra at different temperatures were collected on FLS 980 (Edinburgh). Absolute QY was measured on FLS 920 with an integrating sphere (Edinburgh). Excitation-emission matrix was recorded on a Fluoromax-4 spectrofluorometer (Horiba Jobin-Yvon).

## 3. Results and discussion

### 3.1. A new kind of PCDs with high quantum yield

A facile method was adopted to prepare PCDs with high quantum yield, excellent water solubility and low toxicity, by hydrothermal reaction of PAA and EDA (Fig. 1). The optimal reaction condition was confirmed as 200 °C and 8 h (Table S1). By optimizing the ratio of PAA and EDA (Table S2), a new kind of PCDs was gotten with an absolute quantum yield as high as 44.18% in solution. According to the different characters and wavelengths of emission peaks in PCDs' PL spectra (Fig. 2a), two major fluorescence centers could be distinguished. The fluorescence center 1's optimal excitation and emission wavelengths were respectively at 340 nm and 410 nm (Fig. 2a) with little excitation dependence. However, the fluorescence center 2 was excitation-dependent, whose excitation wavelength started from 380 nm and emission wavelength

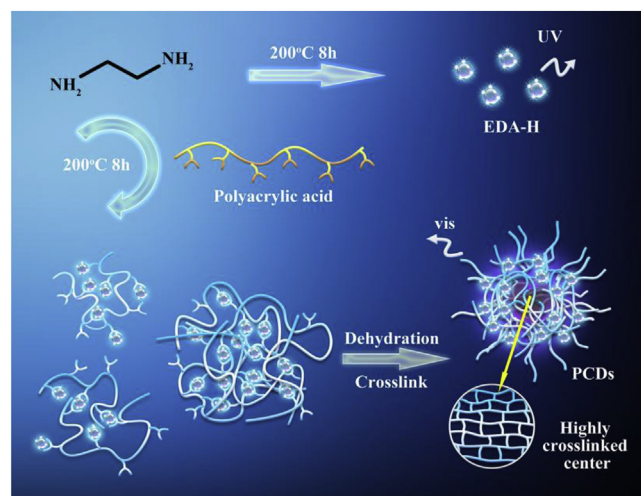


Fig. 1. The schematic diagram of experimental procedure.

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