

Fluorescent Polyurea-Carbon Dots: Preparation, Characterization and Use as Sensor for Doxycycline Detection

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Electronic Supplementary Information

Abstract Fluorescent polyurea-carbon dots (PU-CD) were successfully achieved through a co-pyrolysis technique, combining polyurea (PU) with carboxyl-containing carbon dots (PCD) at a temperature of 220 °C. The PU was fabricated via a simple precipitation polymerization process using toluene diisocyanate in a water/acetone binary solvent system. PCD was generated by thermal treatment of poly(ethylene glycol) (PEG) at the same elevated temperature. To elucidate the structural characteristics of PU-CD, as well as its precursor components PU and PCD, a comprehensive suite of analytical techniques was employed, including transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), dynamic light scattering (DLS) and X-ray photoelectron spectroscopy (XPS). These analyses confirmed the formation of amide bonds resulting from the reaction between the terminal amines of PU and the carboxyl groups of PCD. An in-depth comparison of the fluorescence properties of PU-CD revealed marked enhancements in fluorescence intensity when contrasted with PU, PEG, and the individual PCD. The research explored the impact of various factors such as concentration, pH in aqueous solutions, and solvent type on the fluorescence emission of these materials, providing valuable insights into their emission mechanisms. It was particularly noteworthy that both PCD and PU-CD exhibited a confined-domain crosslink-enhanced emission effect. Utilizing the aqueous dispersion of PU-CD as a fluorescent probe, the detection of doxycycline (DOX), a long-acting, broad-spectrum, semi-synthetic tetracycline antibiotic, was achieved with a detection limit of 2.9×10^{-7} mol/L. This study introduces a simple, green, and cost-effective fluorescent probe for the detection of DOX, which has significant potential for application in the realms of analytical chemistry and food safety monitoring in the future.

Keywords Polyurea; Poly(ethylene glycol); Carbon dots; Doxycycline detection

Citation: Zhou, X. X.; Yin, Y. T.; Zhang, X. Y.; Li, S. S.; Jiang, X. B.; Zhu, X. L.; Kong, X. Z. Fluorescent polyurea-carbon dots: preparation, characterization and use as sensor for doxycycline detection. *Chinese J. Polym. Sci.* 2025, 43, 1792–1803.

INTRODUCTION

Carbon materials, including graphite, fullerenes, carbon nanotubes, and graphene, have attracted significant attention in the field of materials science.^[1,2] Numerous methods have been explored to enhance the fluorescent properties of these materials. Carbon dots (CDs), which are carbon-based quasi-spherical fluorescent nanoparticles ranging from 1 nm to 10 nm in size, have emerged as promising candidates.^[3] These CDs can exist as hybrid carbon structures encompassing both sp^2 and sp^3 configurations, and exhibit single or multilayer graphite structures, or take the form of polymeric aggregates. The discovery of fluorescent carbon nanoparticles dates back to 2004, when they were extracted from the dissociation of carbon nanotubes.^[3] Since then, CDs have garnered increasing interest because of

their exceptional photoluminescence properties. In addition, the rich and adjustable surface functional groups of CDs contribute to their versatility and potential for diverse applications.^[4,5]

Poly(ethylene glycol) (PEG) has garnered approval from the US Food and Drug Administration for a range of biomedical applications owing to its non-toxic, non-immunogenic, and water-soluble nature.^[6] Owing to its straightforward composition, PEG has been extensively explored as a carbon source for CDs, offering enhanced biocompatibility and reduced toxicity.^[7–12] In these processes, PEG is treated by various methods, including hydrothermal treatment,^[4,7] direct heating,^[8] alkalization,^[9] ultrasonication,^[10] transition metal doping,^[11] and microwave.^[12] In our previous work, we investigated the fluorescent properties of PEG^[13–15] and its copolymers with acrylic^[16] and siloxane.^[17] These fluorescent materials have found applications in cell imaging^[13] and sensors.^[14,15,17] Nevertheless, the fluorescence of these materials is constrained by several factors, including the need for an optimal molecu-

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Received March 19, 2025; Accepted June 9, 2025; Published online July 30, 2025

lar weight, preference for shorter excitation wavelengths, and requirement for higher concentrations.^[13–16] This underscores the importance of further research to optimize these parameters and enhance the fluorescence properties of PEG-based materials for various applications.

Currently, CDs have garnered significant research attention, yet reports on the fluorescence properties of polymer/CD composites remain scarce. Polyurea (PU), an emerging fluorescent polymer that lacks the traditional large conjugated structure, is gaining increasing attention. In our previous work, amine-rich PU was successfully synthesized using toluene diisocyanate (TDI) as the monomer in a water/acetone mixture via simple precipitation polymerization.^[18,19] Notably, we discovered that PU exhibits remarkable fluorescence properties.^[20] Given the unique fluorescence characteristics of PU and the potential of CDs, there is a promising opportunity to explore the fluorescence properties of PU/CD composites and their potential applications in various fields.

In this study, polyurea-carbon dots (PU-CD) were synthesized by the co-pyrolysis of PU and carboxyl-functionalized carbon dots (PCD) at 220 °C. PCD was easily obtained by thermally treating PEG with a molecular weight of 400 Da at the same temperature. A comprehensive analysis was conducted to characterize the structural properties of PU-CD, as well as those of its precursor compounds, PU and PCD, in order to determine their chemical composition and structure. This study explored the effects of different factors on the fluorescence characteristics of these hybrid nanomaterials with the goal of understanding the fundamental mechanisms behind

their fluorescence emissions (Fig. 1a). Of significant interest, the water-based dispersion of PU-CD exhibited outstanding potential as a fluorescent sensor for the detection of doxycycline (DOX), a long-acting, broad-spectrum, semi-synthetic tetracycline antibiotic.^[14] The detection limit for DOX was found to be 2.9×10^{-7} mol/L, highlighting the probe's high sensitivity and excellent selectivity. This breakthrough suggests a significant potential for the creation of advanced analytical instruments that can be used for environmental monitoring and detection of DOX in water-based environments.

EXPERIMENTAL

Materials

The PU used in this study was prepared according to our previous work^[18,19] (details are provided in the electronic supplementary information, ESI). The obtained PU exhibited an irregular micron-sized porous particle shape (Fig. S1 in ESI). Polyethylene glycol PEG ($M_n=400$) was purchased from Macklin Chemical. Doxycycline (DOX) and dimethyl sulfoxide (DMSO) were supplied by Aladdin Chemicals and used as-received. Tetrahydrofuran (THF) and ethanol (EtOH) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd. and China National Pharmaceutical Group Chemical Reagent Co., Ltd., respectively. Ultrapure water was obtained from a standard series ultrapure water system (FFX1002-UP, Qingdao Flom Technology Co., Ltd.).

Preparation of PCD and PU-CD

PEG (1.0 g), with a molecular weight of 400, was placed in a crucible and roasted in a tubular furnace. PEG was gradually heat-

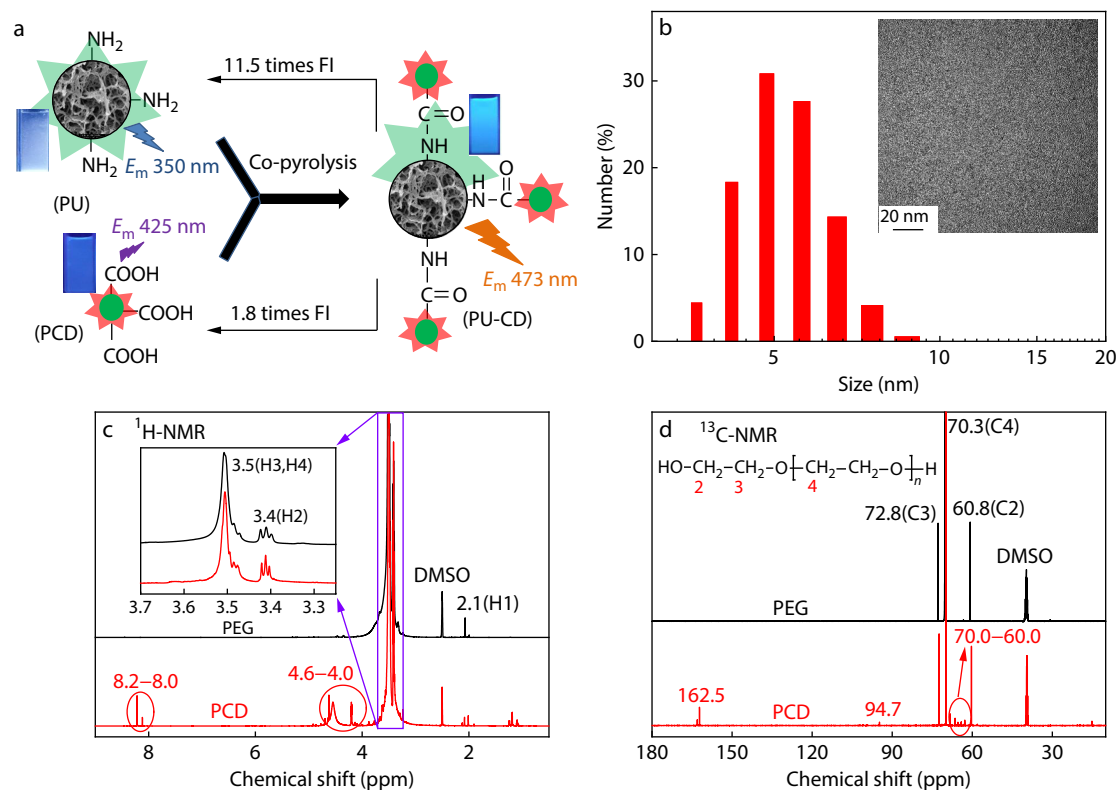


Fig. 1 (a) The formation mechanism of PU-CDs; (b) TEM image and particle size distribution of PCD aqueous solution (2.0 mg/mL); (c) ¹H-NMR and (d) ¹³C-NMR spectra of PEG and PCD.

ed from room temperature to 220 °C at a rate of 5 °C/min. After maintaining this temperature for 0.5 h, it was cooled naturally. This process yielded a yellow liquid, designated as PCD, with a production rate of 96%. A similar approach was adopted to synthesize PU-CD. A mixture of PCD (0.8 g) and PU (0.2 g) was roasted in a tubular furnace under the same conditions as those mentioned earlier.

Characterization

The chemical structures of PU-CD and its precursors, PU and PCD, were thoroughly analyzed by Nuclear Magnetic Resonance (NMR, Advance III, Brüker, USA, 400 MHz) using DMSO- d_6 as the solvent, and by Fourier transform infrared spectroscopy (FTIR, Tensor 27, Brüker, USA) using KBr tablets in the range of 4000–400 cm^{-1} . Transmission electron microscopy (TEM, JEM-1400, JEOL, Japan) was used to visualize the morphology of the materials. The particle size and size distribution of PCD and PU-CD were accurately measured using dynamic light scattering (DLS, Nano-ZS, Malvern, Britain). The samples were characterized using X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher, USA). The crystallization status of the samples was investigated using an X-ray diffractometer (XRD, D8 Focus, Brüker, USA) in the two-theta range of 5° to 50° using a Cu-K α radiation source. The UV absorption spectra of the PCD and PU-CD aqueous solutions were measured using a UV-Vis spectrophotometer (Lambda 35, Perkin Elmer, USA) over a wavelength range of 200–600 nm. The fluorescence emissions of the PCD and PU-CD aqueous solutions were measured using a fluorescence spectrometer (F-7000, Hitachi, Japan). The excitation slit width was set at 2.5 nm, and the emission slit width was set to 1.0 nm.

Detection of DOX

For fluorescence tests, an aqueous solution of PU-CD at 2.0 mg/mL concentration and pH=7 was prepared. The fluorescence emission was also measured for the solution in the presence of DOX at different concentrations. To determine whether the fluorescence emission interfered with commonly known metal ions, the test was conducted in a solution of PU-CD in the absence or presence of DOX with one of the eleven metal ions, including Pb^{2+} , Al^{3+} , Cd^{2+} , Mg^{2+} , Cu^{2+} , Fe^{2+} , Fe^{3+} , Cr^{3+} , Cr^{6+} , Ag^+ , and Na^+ .

RESULTS AND DISCUSSION

Preparation and Characterization of PCD

PEG has been approved by the United States Food and Drug Administration (FDA) for numerous biomedical applications. Consequently, CDs derived from PEG exhibited inherently reduced toxicity and enhanced biocompatibility. Additionally, PEG's remarkable passivation capabilities of PEG facilitate a straightforward, self-passivating, and environmentally friendly synthesis of CDs.^[6] Given the simple structure and accessibility of PEG, coupled with the availability of various PEG series with distinct molecular weights and functionalities, the formation mechanism of PEG-derived CDs has been thoroughly explored and is clearer than that of other CDs.^[8,9,21]

Herein, PCD was synthesized by the pyrolysis of PEG ($M_n=400$) at 220 °C. Investigations into the preparation of PCD using PEG as a carbon source revealed that the formation of carbon dots is a result of the pyrolysis and oxidation process-

es of the PEG chains.^[21] As shown in Fig. S2 (in ESI), carbon free radicals were initially generated by heating, and these radicals were promptly converted into peroxides in the presence of oxygen. Hydroxyl free radicals contribute to the formation of reaction intermediates from the unstable peroxides. Within these intermediates, C—O bonds are cleaved, resulting in the formation of carbonyl compounds and unstable short-chain polymer free radicals. Subsequently, carbon-carbon double bonds were established through dehydration and hydrogen-trapping mechanisms. During this process, olefins (fragments containing carbon-carbon double bonds) coalesce, giving rise to hydrophobic cores. Concurrently, hydrophilic and oxygen-containing fragments, such as hydroxyl, carbonyl, and ether groups, primarily reside on the surface and serve as passivating layers. Ultimately, these processes culminate in the formation of CDs with distinct core-shell structures.^[6,21] The TEM image (Fig. 1b) demonstrates that the nanoparticles obtained through direct carbonization possess an average particle size of approximately 4.0 nm, and DLS analysis of PCD exhibited an average particle size of 4.8 nm and a polydispersity index (PDI) of 0.38. Compared with the PDI of other CDs that have been reported (0.274 to 0.533),^[22–24] the particle size distribution of PCD was at a medium level.

The FTIR spectra of PEG and PCD provided valuable insights into the pyrolysis process (Fig. S3 in ESI). In PEG, the broad peak centred at 3475 cm^{-1} corresponds to the stretching vibration of the O—H bonds.^[25] The peaks observed at 2890 and 1470 cm^{-1} were attributed to the stretching and bending vibrations of the C—H bonds, respectively.^[26] The peak at 1643 cm^{-1} can be assigned to the bending mode of the O—H bonds of PEG and water molecules.^[21] The multiple peaks ranging from 1000 cm^{-1} to 1400 cm^{-1} represent the absorption peaks of the C—O—C stretching vibrations.^[8,27] Upon comparing the FTIR spectra of PEG and PCD, a significant reduction in peak intensities was observed in PCD for various vibrational modes, including C—H stretching, O—H bending, and C—O—C stretching. This decrease in peak strength suggests a substantial reduction in the relative content of the PEG components during carbonization. The emergence of a new peak at 1720 cm^{-1} is noteworthy. The peak at 1720 cm^{-1} corresponds to the stretching vibration of C=O bonds^[8] indicating the formation of carbonyl groups during pyrolysis. The peak at 1643 cm^{-1} was also attributed to the stretching vibration of C=C bonds,^[21,28] suggesting the presence of olefinic fragments in the PCD structure.

Figs. 1(c) and 1(d) present the NMR spectra of PEG and PCD, providing detailed insights into their chemical structures. The chemical structure of PEG is shown in Fig. S4(a) (in ESI), and the corresponding chemical shifts (δ) are listed in Table S1 (in ESI).^[29] In Fig. 1(c), the terminal hydroxyl proton H1 of PEG was clearly observed at 2.1 ppm.^[29] The proton peak of the methylene group H2, which is connected to the terminal hydroxyl group, appears at 3.4 ppm. The δ values of the methylene protons H3 and H4 are centred at 3.5 ppm. Notably, the positions and intensities of these proton peaks remained largely unchanged in the ^1H -NMR spectra of the PCD. This observation suggests that the main structure of PEG is preserved in PCD even after heat treatment. However, several notable differences were observed in the ^1H -NMR spectrum

of PCD. Two sets of new peaks are observed in the spectrum. Peaks located at 8.2–8.0 ppm were attributed to the methanoate end-groups.^[29,30] The peaks between 4.6 ppm and 4.0 ppm are associated with $-\text{CH}_2$ groups that are linked to hydroxyl, ether, or carbonyl functionalities.^[8,29,30]

The ^{13}C -NMR spectrum of PEG (Fig. 1d) exhibited three distinct peaks, reflecting its chemical composition. At 70.3 ppm, C4 represents the methylene carbon, and C3, located at 72.8 ppm, corresponds to the methylene carbon of the terminal group attached to oxygen. The peak at 60.8 ppm belongs to C2, which is the methylene carbon associated with the hydroxyl group.^[31,32] These peaks aligned precisely with the expected chemical structure of PEG, validating its molecular composition. In contrast, the ^{13}C -NMR spectrum of PCD revealed several new peaks, indicating structural modification. The peak at 162.5 ppm is attributed to the ester carbonyl carbon, indicating the presence of an ester functionality in PCD.^[29,31] The peak at 94.7 ppm corresponds to the carbon in the $-\text{O}-\text{CH}_2-\text{O}-$ moiety.^[30] The peaks within the range of 70.0–60.0 ppm are associated with $-\text{CH}_2$ groups linked to ether or carbonyl groups.^[29] These results align with our expectations that molecular chain cleavage and oxidation occur during the carbonization of PEG, leading to the formation of new functional groups, such as double bonds, carbonyls, and ether bonds.

The pH values of the PEG and PCD aqueous solution (2.0 mg/mL) were 7.0 and 5.0, respectively. This decrease in pH indicates that a portion of the hydroxyl groups present on PEG were converted to carboxyl groups during the carbonization process. This observation aligns well with the NMR and FTIR results, providing further evidence for the structural changes undergone by PEG during its transformation into PCD. Based on these findings, it can be inferred that under high-temperature conditions, PEG decomposed into smaller molecular fragments. Subsequently, these fragments underwent carbonization through dehydration reactions, leading to the formation of carbon nuclei.^[33] The hydroxyl groups present on these carbon nuclei undergo oxidation, resulting in the formation of oxygen-containing fragments. These fragments ultimately contribute to the formation of CDs that possess carboxyl or hydroxyl groups on their surface, which is consistent with the literature.^[8]

Preparation and Characterization of PU-CD

According to the preparation method of PCD, the PU was also calcined at 220 °C for 0.5 h. FTIR and NMR spectra of PU before and after heating were compared (Fig. S5 in ESI). It was found that the spectra of the two materials were completely consistent, the absorption peaks of all functional groups and the proton chemical shift did not change, and no new peaks appeared, indicating that the structure of PU was unchanged after treatment at 220 °C. This is consistent with previously reported results that the thermal decomposition of PU occurs only when the temperature is higher than 275 °C.^[18,19] The SEM and TEM images of the PU-CDs indicate that PCD was uniformly embedded in the PU layer (Fig. S6a in ESI), and the PU-CDs exhibited an irregular micron-sized particle shape (Fig. S6b in ESI).

The structure of PU-CD was characterized by FTIR and compared with that of its precursor PCD and PU (Fig. S7 in ESI). In PU spectrum (Fig. S7a in ESI), the broad peaks at 3300 and

1540 cm^{-1} correspond to the stretching and bending vibrations of N—H, respectively. The peak at 1650 cm^{-1} is the stretching vibration peak of C=O and that at 1600 cm^{-1} is the characteristic peak of the benzene ring.^[18–20] In addition, the peak at 1220 cm^{-1} corresponds to the stretching vibration of C—N.^[20,34] Compared with PU, PU-CD not only has an N—H stretching vibration peak at 3300 cm^{-1} , but also an O—H stretching vibration peak at approximately 3475 cm^{-1} , and a C—H stretching vibration absorption peak at 2890 cm^{-1} . By magnifying the absorption peak at 1800–1000 cm^{-1} (Fig. S7b in ESI), it can be seen that PU-CD has the characteristic peaks of PU: 1650 cm^{-1} (urea-carbonyl C=O stretching vibration), 1600 cm^{-1} (benzene ring), 1540 cm^{-1} (N—H bending vibration), and 1220 cm^{-1} (C—N stretching vibration), and has the characteristic peaks of PCD: stretching vibration peak at 1720 cm^{-1} C=O, stretching vibration peak of C=C at 1643 cm^{-1} , C—H bending vibration peak at 1470 cm^{-1} , and stretching vibration of C—O at 1105 cm^{-1} . We speculated that the combination of PCD with PU was achieved through an amide derived from the amine group on PU and the carboxyl group on PCD. However, the carbonyl absorption peak of amide is also approximately 1650 cm^{-1} ,^[35] which overlaps with the carbonyl peak of urea.

It can be seen from ^1H -NMR (Fig. 2a) that, the original peak of methylene (H2, Fig. S4 in ESI) adjoined with the terminal hydroxyl in PEG at 3.4 ppm almost disappeared in PU-CD, while the original peak in PU at 4.8 ppm belonging to the terminal amine group (H5, Fig. S4 in ESI) completely disappeared in PU-CD. At the same time, the proton peaks of PCD attributed to $-\text{CH}_2$ connected to hydroxyl, ether, or carbonyl groups appeared in the range of 4.6–4.0 ppm^[30] in PU-CD.

From their ^{13}C -NMR spectra (Fig. 2b), we know that the peak area of ester group at 162.5 ppm in PU-CD is significantly smaller than that in PCD. At the same time, compared with PU, C9 on $\text{NH}-\text{CO}-\text{NH}$ at 152.8 ppm, and C6 on benzene ring connected to end amine group at 146.2 ppm in PU-CD significantly decreased. A new amide peak appeared at 154.2 ppm^[36] in PU-CD. The peaks between 120.0 ppm and 100.0 ppm are attributed to the benzene ring C (C7, C8) adjoined with C6,^[18] which almost disappear in PU-CD. These results indicate that the amino group at the end of PU reacted with the carboxyl group on PCD after blending and heating, which is consistent with previous reports.^[37] That is, there are covalent amide bonds between PU and PCD.

To verify this result, XPS tests were performed on PU and PU-CD (Fig. 2c). The O content in PU-CD increased relatively, while the N content decreased. To further illustrate their binding energy and valence state, the XPS spectra were deconvoluted separately for C1s, N1s, and O1s (Figs. 2d–2i), with all the peaks assigned and listed in Table S2 (in ESI).

The C 1s spectrum of PU can be divided into three peaks (Fig. 2d), which are 284.6 eV (C—C, C=C), 285.5 eV (C—N), and 288.8 eV ($-\text{NH}-\text{CO}-\text{NH}-$) respectively.^[38,39] After PU and PCD were blended and heated (Fig. 2e), peaks of C in the ether bond (C—O—C) and amide ($-\text{NH}-\text{CO}-$) appear at 286.6 and 288.1 eV respectively.^[40,41] The former indicates that there are ether bonds between CDs in PU-CD, and the latter is due to the amidation of PCD and PU, as depicted in Fig. 1(a).

The N 1s spectrum of PU can be divided into two peaks

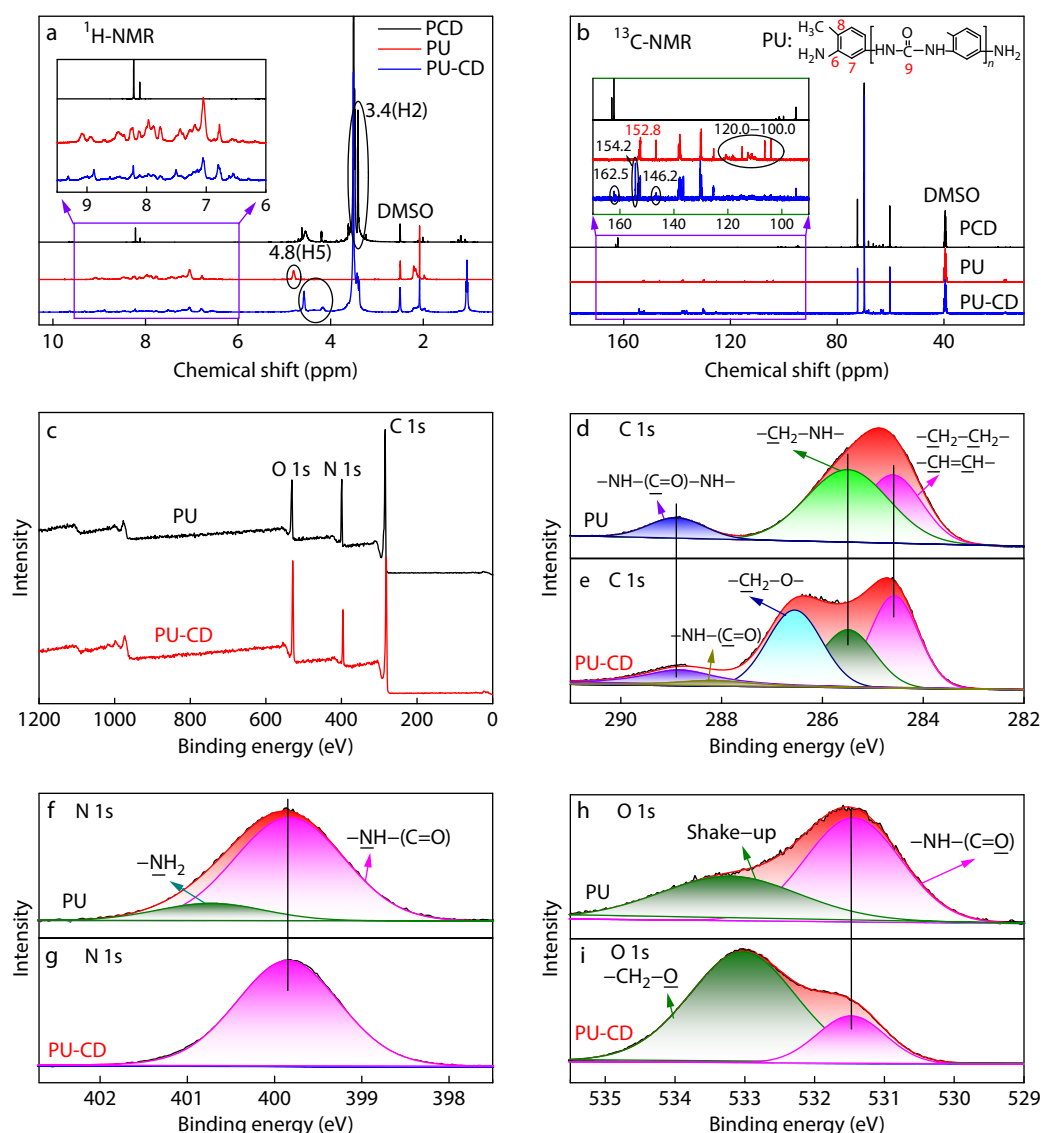


Fig. 2 (a) ^1H -NMR and (b) ^{13}C -NMR spectra of PCD, PU and PU-CD; (c) XPS survey spectra of PU and PU-CD, and the deconvoluted spectra for (d, e) C 1s, (f, g) N 1s and (h, i) O 1s.

(Fig. 2f): the peak of N in the urea group ($\text{NH}-\text{CO}$) at 399.8 eV and the terminal amine ($-\text{NH}_2$) at 400.7 eV.^[41] However, in PU-CD (Fig. 2g), the peak of N of the terminal amine disappeared, and the peak position of N in the urea and amide groups did not change,^[40] indicating that the amine group of PU participated in amidation, which corresponded to the NMR results (Figs. 2a and 2b). Unlike other CDs obtained from the N-containing precursor,^[42–44] PCD obtained with PEG as the precursor did not introduce N-absorption peaks.^[9,10] In addition, the decomposition temperature of polyurea exceeds 330 °C.^[18] During the formation of the PU-CDs, the chemical structure of PU did not change significantly. Only the free amino groups on PU formed amide groups with the carboxyl groups in PCD, as confirmed by NMR (Figs. 2a and 2b). The density of free amino groups on PU was 0.153 mmol/g,^[19] which was significantly different from that of the urea groups. Therefore, the formed amide group is very small compared to the urea group. In addition, it has been report-

ed that the peak position of the amide group is 399.8 eV^[41] and the peak position of the urea group is at 399.9 eV.^[39] The positions of the two are very close. Therefore, only one urea peak was observed in the N 1s spectrum of PU-CD (Fig. 2g). In the O 1s spectrum of PU (Fig. 2h), the peak of the O atom on the urea carbonyl group was located at 531.4 eV. After blending and heating with PCD (Fig. 2i), the peak of O on the ether bond appears at 533.0 eV,^[45] indicating that PCD successfully reacted with PU. Finally, PU and PU-CD were characterized using XRD (Fig. S8 in ESI). As shown in Fig. S8 (in ESI), the XRD patterns of PU and PU-CD showed similar crystallization peaks at 16.11°, 20.92°, and 25.11°,^[18] and the diffraction peaks did not shift, indicating that the crystallization region of PU did not change and that PU and PCD only reacted on the PU surface.

Fluorescent Properties of PCD and PU-CD

Effect of excitation wavelengths (λ_{ex})

Our previous investigations revealed that low-molecular-weight PEG, including the 400 utilized in this study, scarcely exhibits flu-

orescence at low concentrations.^[13–15] Remarkably, Following its conversion into carbon dots, PCD displays notable fluorescent emission.^[8] In the present study, we examined aqueous solutions of PEG and PCD (2.0 mg/mL) under 365 nm UV illuminations. PEG displayed minimal fluorescent emission, whereas PCD exhibited pronounced and vivid blue fluorescence (Fig. S9 in ESI).

The fluorescence emission of the PCD aqueous solution (2.0 mg/mL) was thoroughly investigated at various λ_{ex} as depicted in Fig. 3(a). The results indicate that PCD exhibits exci-

tation-dependent behavior in the excitation range of 260–470 nm. Notably, upon excitation at 260–280 nm, PCD displays a dual-peak emission profile with peaks centered at 330 and 425 nm. We postulate that the emission at 330 nm arises from the clustering of incompletely pyrolyzed PEG within PCD. This aligns well with our previous observations, where PEG exhibited an emission at 340 nm when excited at 280 nm.^[13–15] It is noteworthy that the emission of PCD at 330 nm differs significantly from that of the raw PEG400, which exhibits relatively weaker fluorescence intensity under identi-

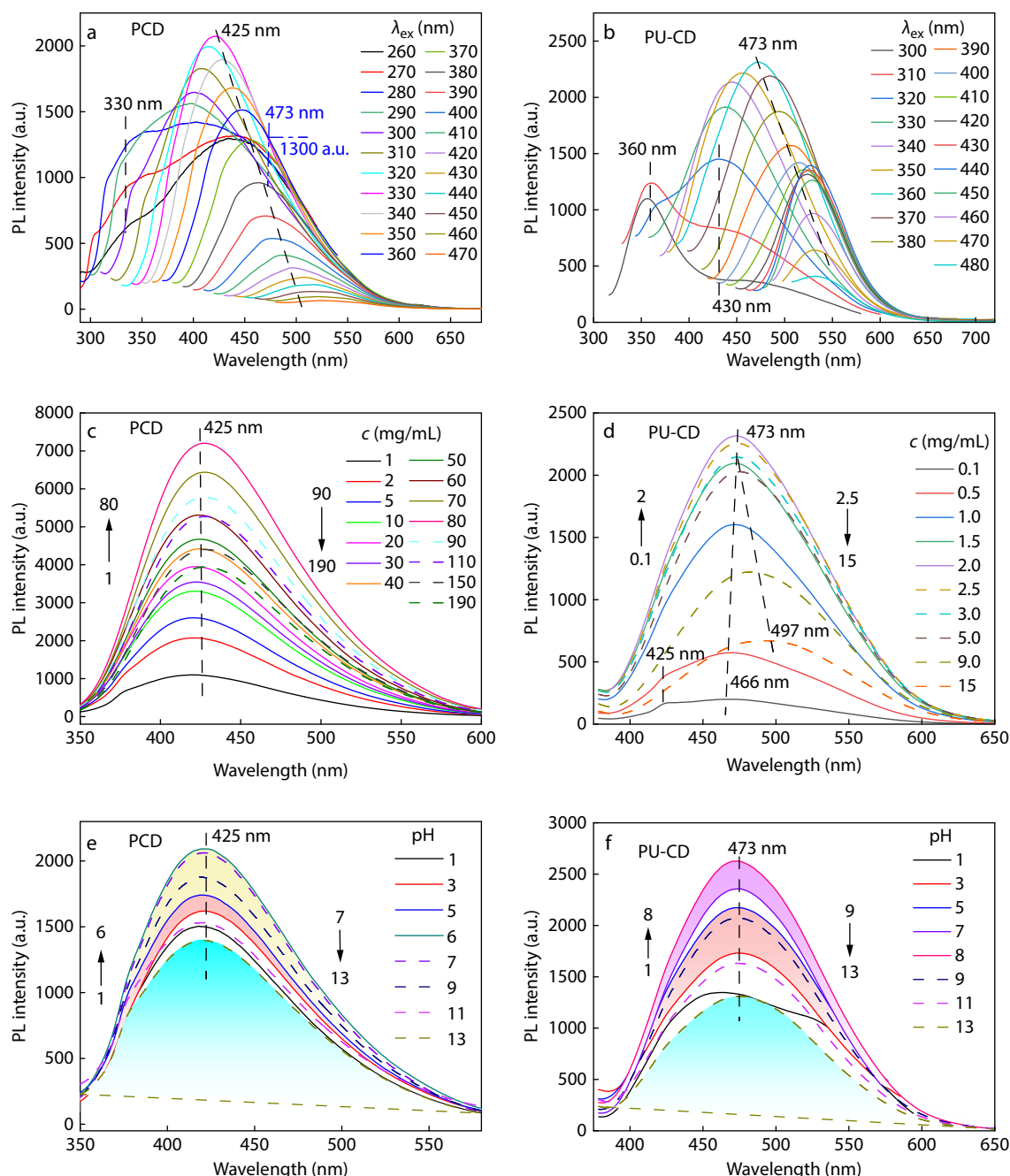


Fig. 3 Fluorescence emission spectra: (a) PCD (2.0 mg/mL) and (b) PU-CD (2.0 mg/mL) aqueous solution at different λ_{ex} ; (c) PCD excited at 330 nm and (d) PU-CD excited at 360 nm with different concentrations (pH=7, 25 °C); (e) PCD excited at 330 nm (2.0 mg/mL) and (f) PU-CD excited at 360 nm (2.0 mg/mL) aqueous solution at varied pH values.

cal excitation conditions (Fig. S10a in ESI). Previous research has shown that PEG only exhibits significant cluster-induced emission when its molecular weight exceeds a critical threshold,^[13] indicating a distinct form of PEG within the PCD compared to raw PEG400. When excited at 260–280 nm, the emission of PCD at 425 nm can potentially be attributed to the self-irradiation of PCD by its own emission at $\lambda_{\text{ex}} = 330$ nm. This hypothesis is supported by the data in Fig. 3(a), which reveal that when PCD is excited at 330 nm, its λ_{em} is also centered at 425 nm. Moreover, it has been reported in the literature that when CD obtained with PEG as the precursor are excited at 330 nm, their emission peak is also at 425 nm.^[10] As λ_{ex} increases to 290–300 nm, the emission profile of PCD gradually transitioned from a dual peak to a broader single peak. A further increase in λ_{ex} from 300 nm to 330 nm results in a gradual increase in fluorescence intensity (FI) accompanied by a red-shift in λ_{em} from 400 nm to 425 nm. However, upon further increasing λ_{ex} , the FI of PCD gradually decreased, and λ_{em} continued to red-shift (Table S3 in ESI).

Numerous scientific reports have shown that CDs synthesized from polymer carbon sources exhibit noteworthy emission properties that stem from the crosslink-enhanced emission (CEE) effect. The densely carbonized framework acts as a physical cross-linking junction, intricately modulating the energy levels and transition pathways of fluorogens or potential chromophores, which would otherwise be non-emissive in isolation. Notably, the CEE effect involves the mitigation of non-radiative transitions, thereby significantly augmenting fluorescence, which is occasionally accompanied by shifts in the emission hues.^[45,46] Consequently, it is unanimously recognized that the fluorescence exhibited by PCDs is predominantly attributed to the CEE phenomenon.

In comparison to the PU aqueous dispersion, the PU-CD aqueous solution (2.0 mg/mL) displayed brighter blue fluorescence under 365 nm UV light irradiation (Fig. S9 in ESI). When the fluorescence emission of the PU-CD solution under varying λ_{ex} was examined (Fig. 3b), a pattern similar to that of PCD was observed. Specifically, when λ_{ex} did not exceed 320 nm, PU-CD exhibited dual emission peaks centered at 360 and 430 nm. As λ_{ex} gradually increased from 330 nm to 360 nm, the emission peak near 360 nm disappeared, while the FI near increased to a peak value of 2313 and red-shifted the emission wavelength (Table S3 in ESI). With further increments in λ_{ex} , the FI of PU-CD began to decline, accompanied by a red-shift in λ_{em} . Under identical excitation conditions (2.0 mg/mL, 360 nm), the FI of PU-CD (2313, 473 nm) surpassed that of PCD by a factor of 1.8 (1300, 473 nm, Fig. 3a) and was 11.5 times higher than that of PU (202, 473 nm, Fig. S10b in ESI). These findings indicate that the incorporation of PCD into the PU matrix significantly boosts the FI of the resulting PU-CD. This remarkable enhancement underscores the exceptional fluorescent properties of PU-CD, providing valuable insights for further research and applications of fluorescent materials.

Effect of concentration

The fluorescence emission spectra of PCD and PU-CD aqueous solutions were recorded at various concentrations under excitation at 330 and 360 nm, respectively (Figs. 3c and 3d). The fluorescence emission spectra of the respective precursors, PEG and

PU, were also recorded at various concentrations under excitation at 290 nm (Fig. S11 in ESI). By comparing Fig. S11(a) (in ESI) and Fig. 3(c), the λ_{em} values of PEG and PCD remained unchanged at 342 and 425 nm, respectively. As shown in Fig. S11(a) (in ESI), the FI of the PEG aqueous solution exhibits a continuous upward trend as the concentration increased from 0.1 mg/mL to 200 mg/mL. However, the PCD aqueous solution exhibited a distinctly different trend (Fig. 3c). Initially, the FI increased with increasing concentration but subsequently decreased gradually (Table S4 in ESI). Specifically, the FI of PCD peaked at 80 mg/mL. Beyond this point, as the concentration further increased, the FI rapidly declined owing to fluorescence self-quenching, a phenomenon commonly observed at high concentrations.^[47,48]

Fig. S11(b) (in ESI) and Fig. 3(d) show the fluorescence emission spectra of PU and PU-CD at concentrations ranging from 0.1 mg/mL to 18 mg/mL excited at 290 and 360 nm, respectively. As shown in Fig. S11(b) (in ESI), the FI of PU gradually increased with increasing concentration, while λ_{em} remained constant at 350 nm. The FI of PU-CD (Fig. 3d) exhibited a pattern similar to that of PCD. Initially, the FI increased with increasing concentration, peaked at a concentration of 2.0 mg/mL, and subsequently tapered off. However, the emission wavelength of PU-CD displayed a red shift from 466 nm to 497 nm (Table S4 in ESI). When the PU-CD concentration was below 0.5 mg/mL, another emission wavelength was observed at 425 nm. The successful attachment of PCD to PU significantly altered the fluorescent properties of the PU-CD, closely mirroring the characteristics of CDs. Therefore, the observed decrease in FI of PU-CD at high concentrations can also be attributed to fluorescence self-quenching. This may be because, at high concentrations, particles are prone to forming clusters owing to the shortened inter-particle distances. The formed clusters often do not emit or emit weaker fluorescence, leading to a decrease in the FI.^[48] Furthermore, because the energy of the first electronically excited singlet state of the clusters is lower than that of the particles, the clusters may quench the fluorescence of the particles through processes such as radiative or resonant energy transfer. Fig. S12 (in ESI) presents images of PCD and PU-CD aqueous solutions of different concentrations under a 365 nm UV lamp. All PCD and PU-CD aqueous solutions displayed blue fluorescence under 365 nm UV lamps. As shown in Fig. S12 (in ESI), the fluorescence intensity changes of the PCD and PU-CD aqueous solutions at different concentrations are consistent with those shown in Figs. 3(c) and 3(d).

These results indicate that when the concentration of PCD solutions reaches a certain level, this concentration range is possibly attributed to the balance of the emission and solution turbidity,^[49] leading to a decrease in FI. As the concentration of the PU-CD solutions increased, the FI intensity declined gradually with the appearance of a red shift. The red shift may be caused by the specific structure of the particles and concentration-mediated scattering phenomena.^[49]

Effect of pH

Previous test results have shown that the pH values of 2.0 mg/mL PEG and PCD aqueous dispersion are 7.0 and 5.0, respectively, and the surface of PCD is rich in carboxyl groups. The effect of pH on the fluorescent properties of the PEG or PCD dis-

person was explored by adding HCl or NaOH solutions to the PEG or PCD solutions and adjusting the pH from 1 to 13 (Fig. S13a in ESI and Fig. 3e). As shown in Fig. S13(a) (in ESI), the fluorescence intensity was constant when the pH of the PEG solution was 10 or below. The emission intensity decreased slightly (by 20%) only when the pH was 11 or higher. This is in good agreement with our previous studies on PEG, that is, the intensity of its maximum fluorescence emission peak is less insensitive to pH changes.^[13]

As shown in Fig. 3(e), under excitation at 330 nm, the fluorescence intensity of PCD exhibits a trend of first increased and then decreased as the pH increased. The fluorescence intensity of PCD reached its maximum when the pH was 6 and decreased by 30% when the pH reached 13. This is consistent with the results of previous reports.^[8,28] Although the fluorescence intensity of PCD changes with pH, the position of its emission peak does not change, indicating that pH does not affect the form of the luminescent center of PCD. Subsequently, the effect of pH on the fluorescence properties of PU and PU-CD was investigated (Fig. S13b in ESI and Fig. 3f). It can be observed in Fig. S13(b) (in ESI), the FI of PU first increased and then decreased significantly (64%) with an increase in pH, and reached its maximum at pH=8. The fluorescence behavior of PU-CD was similar to that of PU and PCD. As the pH changed from acidic to alkaline, λ_{em} of PU-CD remained unchanged, and FI first increased and then decreased significantly (50%).

Generally, the pH sensitivity of CDs is due to the protonation or deprotonation of carboxyl and hydroxyl groups on the surface of CDs in acidic or alkaline environments, which leads to changes in the FI.^[8,28] The significant FI changes of PU are due to the sensitivity of the urea and amine groups of PU. The protonation and deprotonation processes of the functional groups on the surface of PU-CD are the main reasons for the changes in fluorescence intensity.

Effect of solvents

PU-CD exhibit uniform dispersibility in a variety of solvents, including strongly polar solvents such as water and DMSO, as well as weakly polar solvents such as THF and ethanol. Fig. S14 (in ESI) presents images of PU-CD dispersed in different solvents under a 365 nm UV lamp.

Figs. 3(b) and S15(a)–S15(c) (in ESI) illustrate the fluorescence emission spectra of PU-CD dispersed in water, THF, DMSO, and EtOH at a concentration of 2.0 mg/mL as a function of λ_{ex} . The corresponding λ_{em} values are presented in Table S5 (in ESI). PU-CD was dispersed in the four solvents with an optimal excitation wavelength of 360 nm, and its emission red-shifted with increasing excitation wavelength. When λ_{ex} was fixed at 360 nm, the emission peaks of PU-CD dispersed in THF, DMSO, ethanol, and water were located at 436, 448, 449, and 473 nm, respectively. The emission peak position of PU-CD shifts towards the red region as the polarity of the solvent increases. There are reports in the literature where CDs were synthesized using *p*-phenylenediamine, urea, and polyethylene glycol in dimethyl sulfoxide, and then different solvents such as toluene, acetone, DMSO, ethanol, and water were added to achieve fluorescence emission ranging from 454 nm to 505 nm.^[50] They attributed this solvent-induced color change effect to the different polarities of the solvents, simi-

lar to those of organic compounds. Strongly polar solvents (protic solvents) can form strong hydrogen bonds with the surface groups of the CDs, whereas weakly polar solvents (aprotic solvents) interact through dipole-dipole interactions. The combined effect of these interactions alters the absorption spectra, thereby influencing the fluorescence emission. The ability to respond to changes in solvent polarity makes PU-CD a promising candidate for applications in sensing and detection systems, where the identification of different solvents or solvent mixtures is crucial.

DOX Detection

Doxycycline (DOX) is well known for its potent bactericidal and antibacterial properties, making it a common choice to prevent and control infections in animal and aquatic products. However, misuse can result in drug residue levels in animal-derived foods exceeding safety standards, thereby posing a risk to consumer health. Consequently, the issue of doxycycline residues has garnered considerable attention. To address this, we examined the fluorescence properties of a PU-CD (2.0 mg/mL) water dispersion following its interaction with DOX (Fig. S16 in ESI). The drug concentration used was 0.5 mmol/L. As depicted in Fig. S16 (in ESI), DOX does not exhibit fluorescence when excited at 360 nm. The addition of DOX to PU-CD quenched its fluorescence intensity by 85%. Based on these findings, we propose that PU-CD has promising potential for the detection of DOX residues.

A set of binary solutions, with PU-CD kept at 2.0 mg/mL while DOX concentration varied, were prepared, and their emission was tested. The results shown in Fig. 4(a) indicate that the emission intensity of the solutions decreased regularly with increasing DOX concentration ([DOX]). Good linearity was observed between the emission intensity (*I*) and [DOX] when [DOX] was not higher than 0.07 mmol/L. Data fitting enabled the establishment of a linear relationship between the emission intensity (*I*) and [DOX] (mmol/L), that is, $I = 2329 - 9991 \times [\text{DOX}]$ with a correlation coefficient $R^2 = 0.9916$ (Fig. 4b). From this linearity, K_{sv} was obtained (6.08×10^3 L/mol) from the equation $I_0/I = 1 + K_{sv} \times [\text{DOX}]$.^[17,51] K_{sv} is a constant factor relative to the quenching efficiency of DOX against PU-CD emission (Fig. 4b). The detection limit (DL) was obtained from the commonly known equation: $\text{DL} = K \times \sigma/S$,^[13,14,17] where, *K* is a numerical factor (for which 3 is usually considered to have a confidence level of 99.9%), σ is the standard deviation of the blank samples from at least 20 measurements (0.96), and *S* is the slope of the linear curve of emission intensity versus [DOX] (i.e., 9991). The DL thus determined was 2.9×10^{-7} mol/L, which is similar to the reported values for DOX (Table S6 in ESI).^[11,14,51–54] We also tested the effect of DOX on PCD (Fig. S17 in ESI), the DL of PCD for DOX was 1.7×10^{-6} mol/L, indicating that PCD was less effective in detecting DOX than PU-CD. Second, PU-CD can be easily separated from the detection system by centrifugation, which is another advantage over PCD.

There are a variety of metal ions in a real environment, which may affect the accuracy of DOX detection. To evaluate the applicability of PU-CD as the probe, DOX detection through PU-CD fluorescence emission was then carried out using aqueous PU-CD solution (2.0 mg/mL) in the presence of eleven common metal ions (Pb^{2+} , Mg^{2+} , Cd^{2+} , Cu^{2+} , Ag^+ , Al^{3+} , Na^+ , Cr^{3+} , Fe^{2+} , Fe^{3+} , and Cr^{6+}). As shown in Fig. S18 (in ESI), in

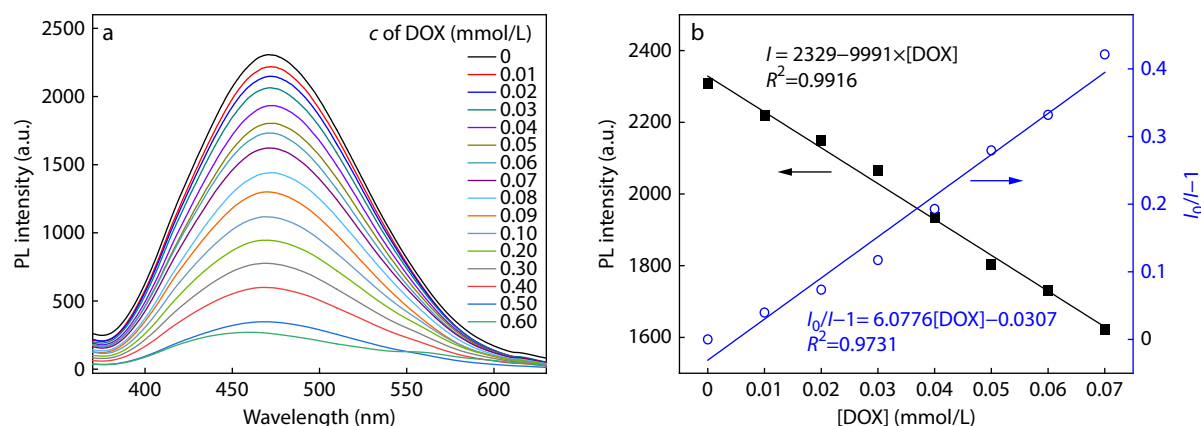


Fig. 4 (a) Fluorescence emission spectra of PU-CD (2.0 mg/mL, λ_{ex} =360 nm) with varied [DOX]; (b) Linearity fitting curve (■) of the PU-CD emission intensity versus [DOX] and the plot (○) of $(I_0/I-1)$ versus [DOX] in the range of 0–0.07 mmol/L, where I and I_0 represent the fluorescence intensity of PU-CD in the presence and absence of DOX, respectively.

the presence of each ion exclusively at a relatively high concentration (0.5 mmol/L), the fluorescence emission of PU-CD was not significantly decreased for all the tested ions, except for two of them, that is, Fe^{3+} and Cr^{6+} , where the emission was lowered to approximately 54% for Fe^{3+} , and to 50% for Cr^{6+} . The addition of DOX (0.5 mmol/L) to PU-CD quenched its fluorescence intensity by 85%. In addition, a ternary solution was prepared by adding every metal ion to the PU-CD-DOX (0.5 mmol/L) solution. The fluorescence emission test results revealed that in the presence of ions, the fluorescence intensity also decreased to below 85% in the PU-CD-DOX solutions (Fig. S18 in ESI). Note that this decrease in emission intensity was detected in the presence of ions at high concentrations. In a real sample, the presence of ions at high concentrations is not common,^[14] which indicates that the effect imposed by the ions is quite limited. These results indicate that the tested ions did not interfere with DOX detection.

To further verify the influence of pH, the emission intensity of PU-CD (2.0 mg/mL), with or without DOX (0.5 mmol/L), was tested at different pH values (Fig. S19 in ESI). These results indicate that within a wide pH range of 3–9, DOX has a fluorescence quenching effect on PU-CD. After adding the same amount of DOX (0.5 mmol/L), its fluorescence decreased by 85%, 87%, 85% and 83% respectively, and there was no significant difference. Considering that the fluorescence intensity of PU-CD is maximum at pH=7, we chose pH=7 for DOX detection.

The fluorescence intensity decreased after the addition of DOX to the PU-CD dispersion solution, which may be caused by the formation of non-luminous ground-state complexes between DOX and PU-CD or the fluorescence resonance energy transfer or charge transfer between them. The interaction between PU-CD and DOX is reflected in the FTIR spectra. Therefore, the infrared characterization of PU-CD and its mixed solution with DOX at different concentrations was performed (Fig. S20 in ESI). The most obvious observation is the rapid decline of the broad band of $-\text{OH}$ at 3360 cm^{-1} in the presence of DOX in the PU-CD-DOX binary solution (Fig. S20a in ESI). This rapid decline of the band is considered to be evidence of certain interactions between DOX molecules and PU-CD through the urea and the hydroxyl oxygen atoms of

PU-CD and the hydroxyl oxygen atoms of DOX molecules. The results showed that the stretching vibration at 1643 cm^{-1} of urea-carbonyl $\text{C}=\text{O}$ in the PU-CD molecular chain and the stretching vibration absorption peak of $\text{C}-\text{O}$ at 1105 cm^{-1} in PU-CD were most affected after DOX addition. As shown in Figs. S20(b) and S20(c), with an increase in DOX concentration, the stretching vibration of urea-carbonyl $\text{C}=\text{O}$ in the PU-CD molecular chain redshifts from 1643 cm^{-1} to 1632 cm^{-1} , and the stretching vibration absorption peak of $\text{C}-\text{O}$ on the PCD redshifts from 1105 cm^{-1} to 1100 cm^{-1} . The results showed that with an increase in DOX content, the electron cloud density around the two sites gradually decreased, which was caused by the transfer of carbonyl groups on the urea group or amide group and some electrons on the carbon-oxygen bond to DOX molecules, resulting in the weakening of the fluorescence intensity of PU-CD and even fluorescence quenching.

NMR spectra of PU-CD and its mixed solution with DOX were obtained (Fig. S21 in ESI). As DOX (0.5 mmol/L) quenched the fluorescence of the PU-CD aqueous solution (2.0 mg/mL), the chemical shift value of the PU-CD atom was small because the drug content was too low. It can be observed in Fig. S21(a) (in ESI), 4.57 ppm in PU-CD is attributed to the shift of the proton peak to a high chemical shift (low field) on the methylene dioxy group because the methylene dioxy group is an electron donor group, and the dimethylamino group and carbonyl group in DOX (Fig. S22 in ESI) are electron-withdrawing groups, so some electrons in the dimethyldioxy group are transferred to the dimethylamino and carbonyl groups. The density of the electron cloud around the methylene dioxy group was reduced, and its resonance peak shifted to a lower field. ^{13}C -NMR spectra (Fig. S21b in ESI) indicated that the formant of C on the urea and amide groups at about 154.24 ppm in PU-CD moves to about 154.26 ppm, and the formant of carbon on the methylene dioxy group at 94.7 ppm also moves to high chemical shift (low field). This is in line with the results of the hydrogen spectrum, which show that the urea, amide, and methylene dioxy groups are all electron donor groups. After blending PU-CD with DOX, electron transfer from the group to DOX reduced the electron cloud density around the group, and its

intensity shifted to a lower field. Therefore, specifically, DOX-induced fluorescence quenching of PU-CD is mainly caused by the formation of non-luminous ground-state complexes of ureyl, amide, or methylene dioxy groups on the surface of DOX and PU-CD and the charge transfer between DOX and excited molecules of PU-CD.

CONCLUSIONS

In this study, PEG was initially used as the carbon source to prepare PCD in a one-step direct heating process, and the formation mechanism of PCD was explored through structural characterization. The results indicate that under high temperatures, PEG first decomposes into fragment molecules, which then undergo dehydration to carbonize and polymerize, forming carbon cores. The hydroxyl groups are oxidized to form oxygen-containing fragment molecules, resulting in carbon dots with carboxyl or hydroxyl groups on their surfaces. Subsequently, the functional groups (carboxyl groups) on the surface of the carbon dots were utilized to form covalent bonds with PU (terminated with amine groups) for surface modification, yielding composite materials with diverse fluorescence properties. The luminescence behavior of PCD and PU-CD was investigated. Compared with PCD and PU, the fluorescence intensity of the composite material was 12 times that of PU and 2 times that of PCD at the same concentration, indicating an enhancement in the fluorescence intensity of PU-CD. Studies on the luminescent mechanisms of PCD and PU-CD revealed that the luminescence behavior change of PCD was due to the cross-linking enhanced emission (CEE) effect. Meanwhile, the fluorescence intensity increase of PU-CD was attributed to the CEE effect, which enhanced luminescence by inhibiting the movement of linked fluorophores. The fluorescence emission wavelength and intensity of PCD and PU-CD were also influenced by factors such as concentration, pH, and solvent. Additionally, PU-CD exhibited selective quenching of doxycycline in the presence of competing metal ions, demonstrating good response sensitivity. Owing to the simplicity and low cost of the detection method, PU-CD can be used for drug detection.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3395-6>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGMENTS

This work was financially supported by the Nature Science

Foundation of Shandong Province, China (Nos. ZR2022MB051 and ZR2021MB112), Science and Technology Bureau of Jinan City (No. 2021GXRC105), Postdoctoral Science Foundation of China (No. 2022M712343), Jinan City University Integration Development Strategy Project (No. JNSX2024030), and a key laboratory of special functional aggregates of the Ministry of Education, Shandong University (No. JJT-2023-02).

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