

Electronic Supporting Information

for

Highly selective detection of phosphate in very complicate matrixes with an off-on fluorescence probe of europium-adjusted carbon dots**

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Experimental Details

Apparatus

The fluorescence and the absorption spectra were recorded with a Hitachi F-2500 fluorescence spectrophotometer (Tokyo, Japan) and a Hitachi UV-3010 spectrophotometer (Tokyo, Japan), respectively. The morphology of CDs was observed on Tecnai G² F20 S-TWIN high resolution transmission electron microscope (HRTEM) (FEI, USA) and Nanoscope Quadrex atom force microscope (AFM) (Veeco, USA). Infrared spectrum (IR) was taken on an IR spectrophotometer (PerkinElmer) and the fluorescence lifetimes were measured with a FL-TCSPEC fluorescence spectrophotometer (Horiba Jobin Yvon Inc, France). The CDs was prepared using Sfire-8-12 muffle furnace (Wuhan, China) for heating at a rate of 10°C min⁻¹, while the photographs were caught with an Olympus E-510 digital camera (Tokyo, Japan). A Fangzhong PHS-3C digital pH meter (Chengdu, China) was used to measure the pH values of the aqueous solutions and a vortex mixer QL-901 (Haimen, China) was used to blend the solution.

Reagents.

The CDs was prepared following the citrate unit employed as the source of carbon while ammonium attached as the surface modifier, where citrate and 11-aminoundecanoic acid were commercially obtained



from Chongqing Dong Fang Chemical Reagents Co., Ltd (Chongqing, China) and Sigma (Alorich, USA), respectively. $\text{Eu}(\text{NO}_3)_3$ with the purity of 99.99% was commercially obtained from Shanghai Maikun Chemical Reagents Co., Ltd (Shanghai, China,.) and its stock solution of $6.0 \times 10^{-3} \text{ mol L}^{-1}$ was prepared and stored at 0-4°C. The working solutions were then prepared by appropriate dilution of this stock solution. Sodium phosphate was purchased from Chongqing Chemical Reagents Co., (Chongqing, China) and $5.0 \times 10^{-3} \text{ mol L}^{-1}$ of stock solution was prepared by dissolving the crystals. Tris-HCl buffer was disposed and adjusted in advance to control the acidity. All other reagents were of analytical grade and were used without further purification. Ultra-pure water (17.8M Ω , LD-50G-E Ultra-Pure Water System, Lidi Modern Waters Equipments Co., Chongqing, China) was used throughout the experiment.

Synthesis of carbon dots (CDs)

Surface-functionalized carbogenic nanoparticles were synthesized according to the literature¹ with slight modification. Briefly, 2.0 g of $\text{H}_2\text{N}(\text{CH}_2)_{10}\text{COOH}$ was at first dissolved in 25.0 mL water with another addition of 0.45 g NaOH for neutralization. After filtered to discard the precipitation, 25.0 mL aqueous solution containing 2.0 g citric acid was added in. Stirred vigorously for a few minutes, thick white precipitation appeared. After filtered to collect sediment and partially dried at room temperature for one day, the resulting wet paste was further dried at 85°C for 2h. The dried product was crashed into a fine powder and then was heated at a heating rate of 10°C min⁻¹ to 300°C using a muffle oven, maintained at this temperature for 2 h before the cessation of heating and cooled to room temperature naturally.

The crude product was dissolved with 25.0 mL hot water by ultrasonic, then centrifuged to remove insoluble particles and collected the supernatant. The pH of the latter was adjusted to 2.0 with 37% HCl yielding a bulk precipitate that was rinsed with water and suspended in 25.0 mL water. Added 0.2 g NaOH to make it dissolve completely and then centrifuged to remove minor insoluble materials. Finally, the deep brown colloidal dispersion solution was obtained. Used the weighing method to get the final concentration of carbon dots was about 27.0 g L⁻¹.

The characterization of the CDs

For the carbon dots, the citrate provides the source for the carbon core while the amino carboxylate serves as the surface modifier. The absorption and emission spectra of the water-soluble CDs was displayed (Fig. S1, ESI†). The amide linkages (-NHCO-) tethering the undecanoate corona covalent to the surface of the citrate-derived carbogenic core is verified by the IR spectrum (Fig. S2, ESI†)². The strong, sharp peaks at $\nu_{\max}/\text{cm}^{-1}$ -1650 and -1560 suggest of -COOH and the peaks at $\nu_{\max}/\text{cm}^{-1}$ -2850, -2925 indicate the existing of -CH₂- as well as a sharp peak at $\nu_{\max}/\text{cm}^{-1}$ -1700 characteristic of amide linkages.

General procedure.

50.0 μL CDs solution and 50.0 μL Tris-HCl buffer solution (pH 7.8) were added to a 1.5-mL microtube. Then 50.0 μL the Eu³⁺ working solution was added, the mixture was vortexed thoroughly and incubated for 15 minutes. Subsequently, the appropriate amount of Pi solution was added, vortex-mixed and placed for another 15min. At last, the solution was diluted to the total volume of 500.0 μL before these measurements.

The fluorescence spectrum was recorded at the F-2500 spectrophotometer by fitting the excitation wavelengths at 360.0 nm, during which the spectral bandwidths were kept at 5.0 nm. Fluorescence intensity was measured at 420.0 nm.

Procedure for the Artificial Wetlands (AWs) water samples

The Artificial Wetlands (AWs) water samples were obtained from the effluent of one Artificial Wetlands system located in the Southwest University, China. The AWs I and AWs II were collected from the Artificial Wetlands exit and Artificial Wetlands entrance, respectively. All the AWs water samples were filtered through 0.45 μm membrane, then diluted and detected according to the general procedure with five replicates for each sample. In order to evaluate the accuracy of the proposed method, other quantities of standard Pi were added to the samples solution for recovery tests.

References

- 1 A. B. Bourlinos, A. Stassinopoulos, D. Anglos, R. Zboril, V. Georgakilas and E. P. Giannelis, *Chem. Mater.*, **2008**, *20*, 4539-4541.
- 2 [L. Tian, D. Ghosh, W. Chen, S. Pradhan, X. J. Chang and S. W. Chen, *Chem. Mater.*, **2009**, *21*, 2803-2809.](#)

Figures

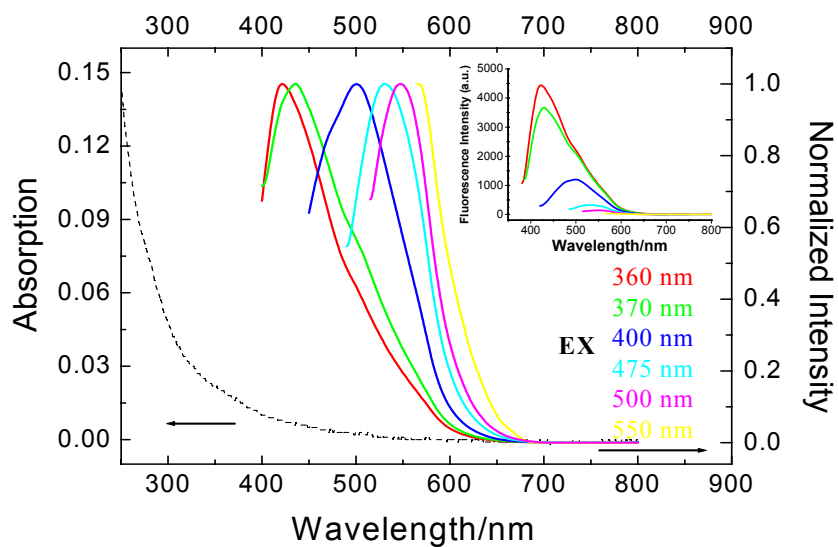


Fig. S1 Absorption (dashed line) and normalized fluorescence spectra of CDs in water at different excitation wavelengths (solid lines). Inset, the fluorescence emission spectra of the CDs at different excitation wavelengths. CDs, 0.015 mg mL^{-1} .

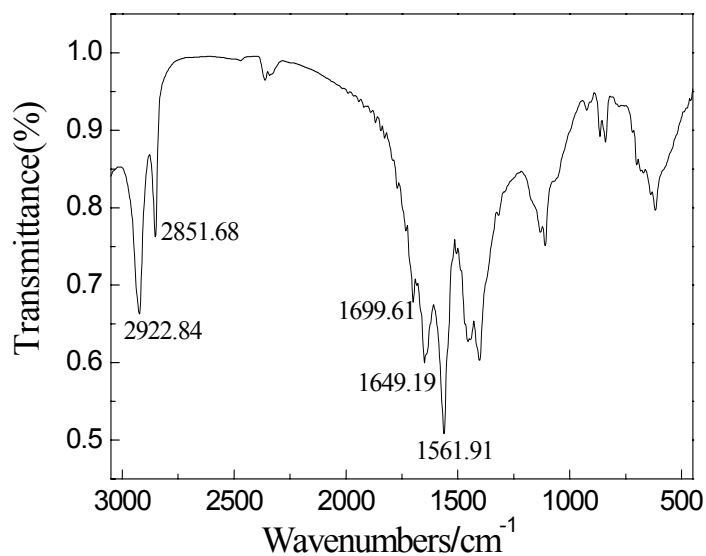


Fig. S2 The IR spectrum of CDs.

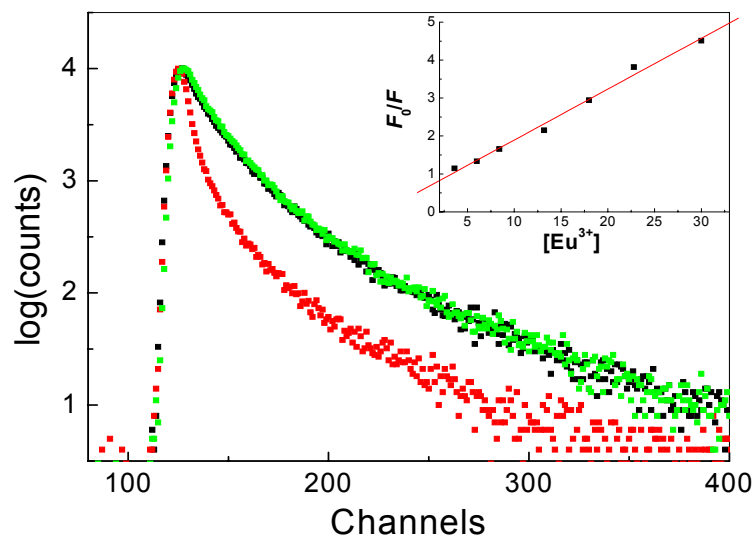


Fig. S3 Fluorescence decay of CDs induced by Eu³⁺, and the fluorescence recovery when Pi added. The black curve stands for the CDs alone, while the red one for CDs-Eu³⁺, the green one for CDs-Eu³⁺ in the present of Pi. CDs, 0.01 mg mL⁻¹; Eu³⁺, 30.0 μM; Pi, 30.0 μM; The insert shows experimental quenching data: the Stern-Volmer plots of F_0/F measured at 420.0 nm versus the Eu³⁺ concentration, which has a good line fit with the correlation coefficient of 0.9955. F_0 and F are the fluorescence intensity of CDs in the absence and presence of the quencher of Eu³⁺ at a certain concentration, Tris-HCl buffer pH 7.8.

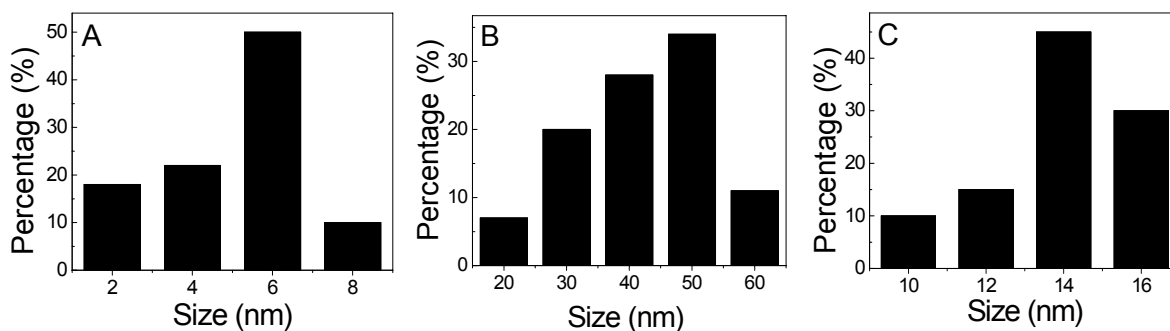


Fig. S4 Size distributions for (A) CDs alone; (B) CDs-Eu³⁺ aggregation; (C) CDs-Eu³⁺ aggregation in the present of Pi.

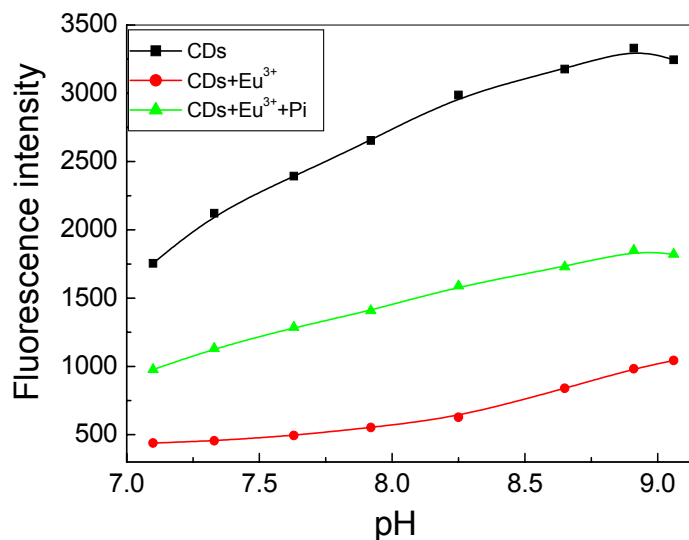


Fig. S5 Influence of pH on the fluorescence recovering effect in the pH range 7.1-9.1. The black curve stands for the CDs alone, while the red one for CDs-Eu³⁺, and the green one for CDs-Eu³⁺ in the presence of Pi. Concentration: CDs, 0.01 mg mL⁻¹; Eu³⁺, 30.0 μM; Pi, 30.0 μM. λ_{ex}, 360.0 nm; λ_{em}, 420.0 nm. All data were collected at 420.0 nm.

Table S1.

Results for the determinations of phosphate in Artificial wetlands water samples

Sample	Pi (× 10 ⁻⁶ M)				Recovery (%, n=5)
	The present method mean ^a ± SD ^b	Molybdenum-blue method mean ± SD	added	Found	
AWs I	16.32 ± 0.36	16.23 ± 0.26	5.0	4.96 ± 0.16	96.0 ~ 102.4
AWs II	60.76 ± 0.65	62.25 ± 0.36	20.0	19.52 ± 0.36	95.8 ~ 99.4

^a Mean of three determinations; ^b SD, standard deviation.

Concentration: CDs, 0.01 mg mL⁻¹; Eu³⁺, 30 μM; Tris-HCl buffer pH 7.8.