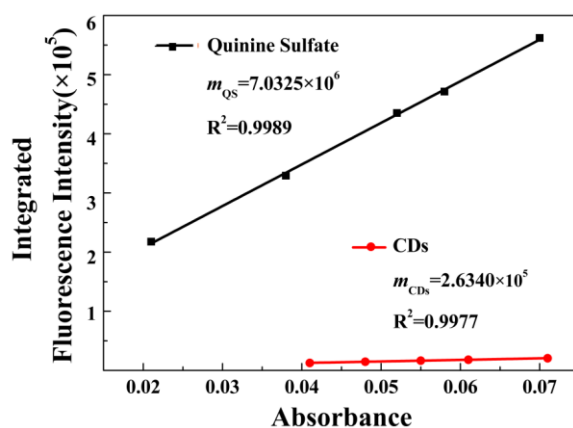


# Supporting information for

## Synthesis of the Cu-Doped Dual-Emission Fluorescent Carbon Dots and Its Analytical Application

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**Figure S1.** The fluorescence quantum yield standard curves for the CDs and quinine sulfate.

### S1 Optimization process of CDs.

To obtain the best optical properties CDs, five factors were considered in the synthesis process.

### 1) The ratio of reactants

When adding an appropriate amount of copper ions, excited state electrons can transfer to the corresponding copper level. So the ratio of raw materials was optimized and the result was shown in Figure S2a. When the ratio of PAN/Cu<sup>2+</sup> is 1:0, 1:0.5, 1:1 and 1:6, respectively, no dual-emission emerges. However, as the ratios are 1:1.5, 1:2, 1:2.5 and 1:3, the carbon dots are dual-emissive. As copper content is lower, copper cannot be successfully doped into the carbon dots. However, excessive copper will lead to surface defects blockage resulting in fluorescence intensity decrease and dual-emission disappearance<sup>[1]</sup>. When the ratio is 1:2, two emission peaks' intensity is the nearest, which benefits the CDs' analysis application. Moreover, the yield of product is the highest with 1:2 ratio. So 1:2 was chosen as the optimal ratio to prepare the CDs.

### 2) Solvent

Solvent is one of the key factors affecting the properties of carbon dots (Figure S2b). As the relative content of ultrapure water increases, the FL intensity, the stability and the yield of carbon dots reduce. It may be due to the water-insolubility of precursor PAN. The fluorescence intensity decrease was also caused by high oxygen content resulting in inefficient electrons and holes recombination and the less radiation recombination<sup>[2]</sup>. Thus, anhydrous ethanol was chosen as the optimal solvent.

### 3) pH

The pH of system can bring great impact on the dual-emission (Figure S2c). When adding acids or bases into the reactant, the CDs dual-emission almost disappears. Acids or bases can

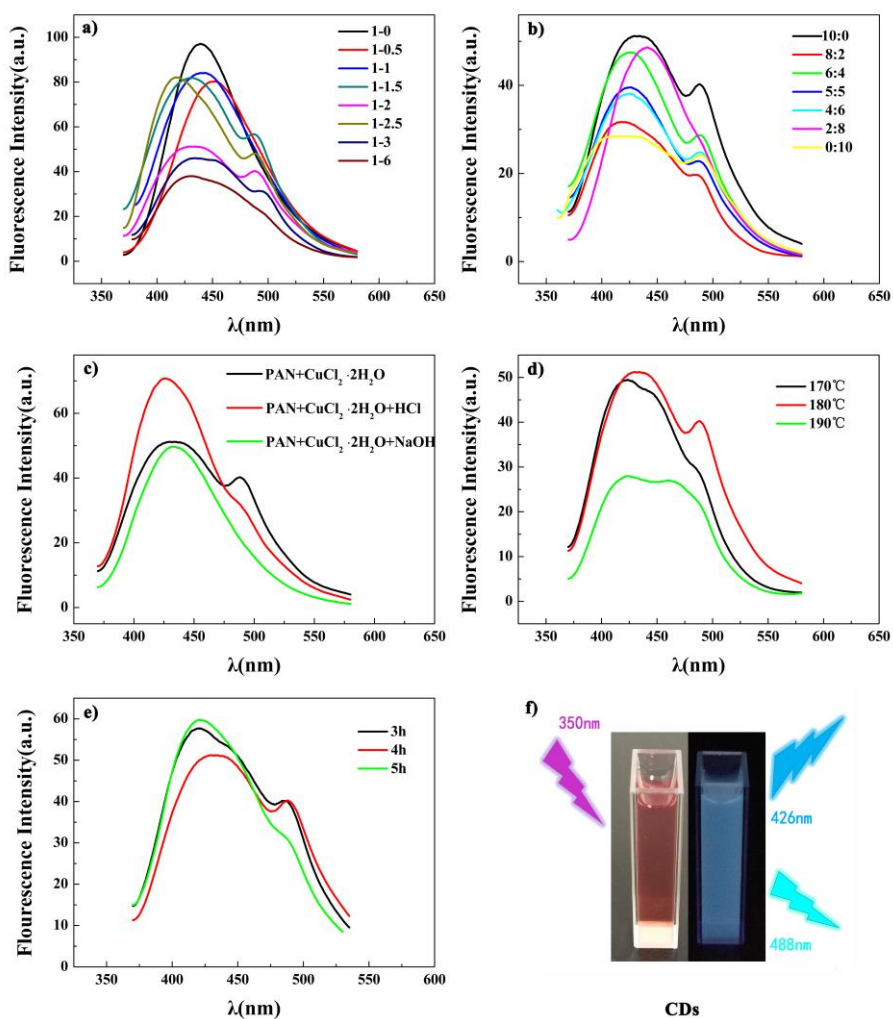
damage the structure of carbon dots easily. Therefore, no acid or base was used in the preparation of dual-mission CDs.

#### 4) Temperature

To obtain good optical properties, the temperature was also optimized (Figure S2d). The experimental result shows that the dual-peak of CDs prepared at 180 °C is the most obvious and the fluorescence intensity is the strongest. Because copper is not successfully doped into the carbon dots at the lower temperature and the surface state of the carbon dots would be destroyed when the temperature is higher than 180 °C<sup>[3]</sup>. So 180 °C was selected as the optimum synthesis temperature.

#### 5) Time

Figure S2e shows that the effects of reaction time on the FL of CDs. The dual-emission characteristic is the most obvious at 4h. Although the 488 nm peak intensity of 3 h synthesis time is almost equal to that of 4 h, the valley of the latter is lower. It is owing to the uniform surface defects at 4h and the destroyed surface state over 4h<sup>[3]</sup>. As a result, 4h was chosen.

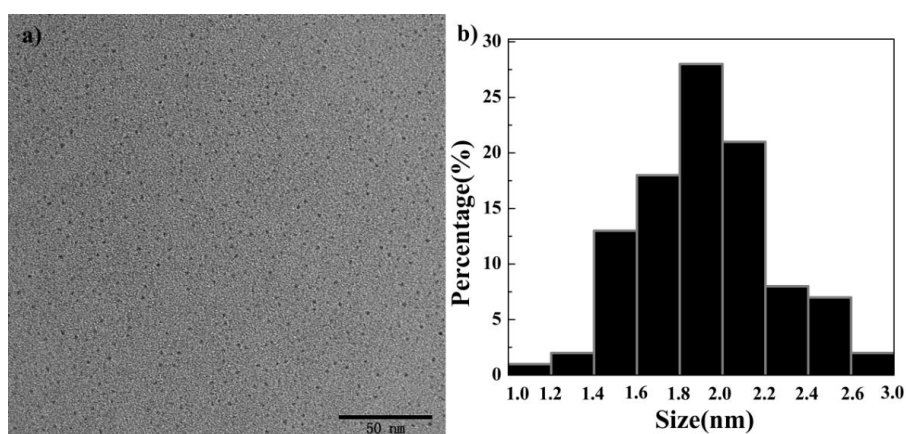


**Figure S2.** Effect of a) raw material ratio, b) ratio of ethanol and ultrapure water, c) 200 μL hydrochloric acid (12 mol/L) or 100 mg sodium hydroxide solid, d) synthesis temperature and e) synthesis time on FL spectra. (The emission spectra were all excited at 350 nm and the concentrations of CDs are same). f) The CDs of the optimal condition in day light and UV light.

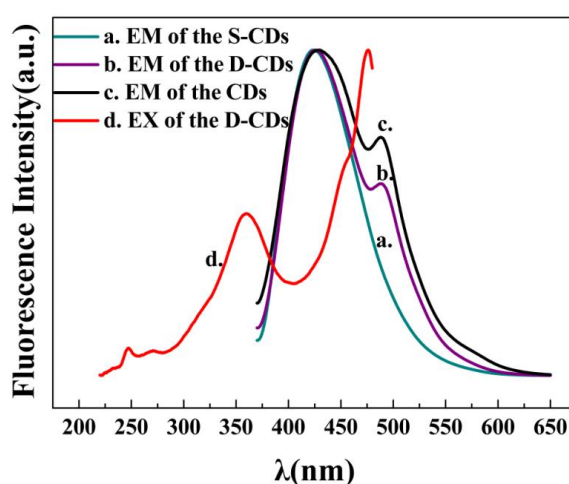
## S2 Synthesis and purification process of P-CDs.

1-(2-pyridylazo)-2-naphthol (49.85 mg) was dissolved in 10 mL ethanol. After 20 min ultrasonic treatment, the solution was transferred to a 25 mL Teflon autoclave and heated at

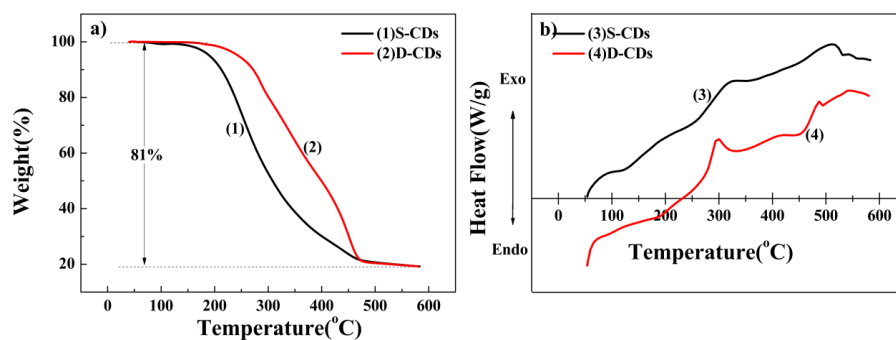
180 °C for 4 h. The product was cooled to room temperature and purified with a silica column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (10:1, v/v') as eluents, and then dried under vacuum after solvent evaporating. The solid CDs were used for characterization and dissolved in ethanol for subsequent fluorescence detection.



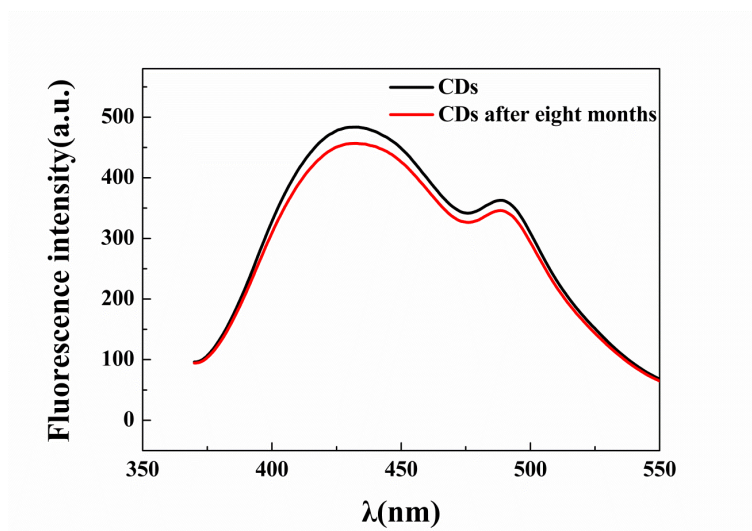
**Figure S3.** a) The TEM image and b) particle size distributions histogram of the single-CDs (S-CDs).



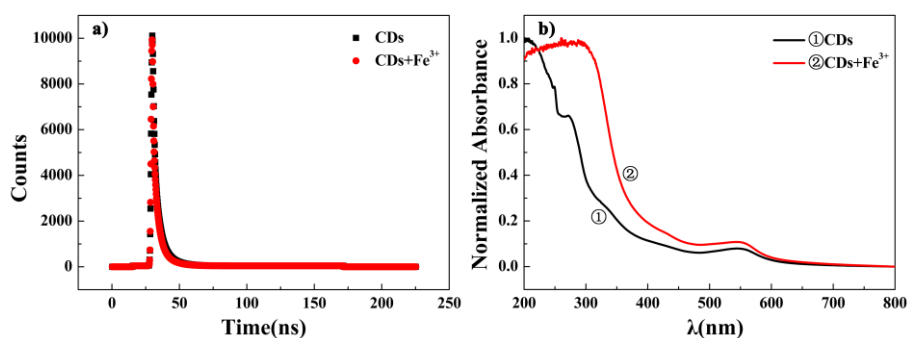
**Figure S4.** The FL spectra of the carbon dots and the excitation spectrum of the D-CDs. (CDs refer to the carbon nanoparticles which are not separated).



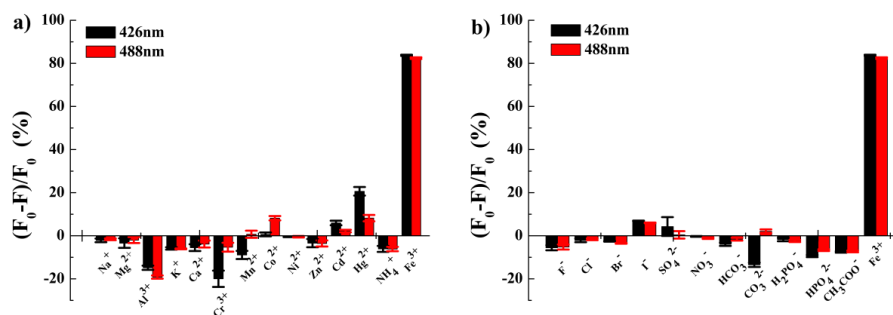
**Figure S5.** a) Thermogravimetric Analysis (TGA) trace and b) Differential Scanning Calorimetry (DSC) profile of the carbon dots.



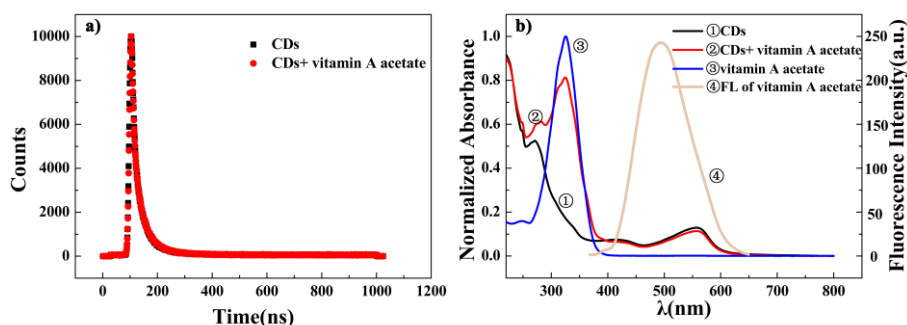
**Figure S6.** The change of CDs FL Spectra after eight month storage.



**Figure S7.** a) Fluorescence lifetime intensity decay of CDs without  $\text{Fe}^{3+}$  and with  $\text{Fe}^{3+}$ . (The fluorescence lifetime of CDs is 4.39 ns, the fluorescence lifetime of complexes is 3.00 ns.) b) Normalized absorption of CDs without  $\text{Fe}^{3+}$  and with  $\text{Fe}^{3+}$ .



**Figure S8.** Effects on the FL intensity of the CDs with a) different cation and b) different anions (all of ions' concentration were 5mol/L).



**Figure S9.** a) Fluorescence lifetime intensity decay of CDs without vitamin A acetate and with vitamin A acetate. (The fluorescence lifetime of CDs is 3.45 ns, the fluorescence lifetime of complexes is 3.58 ns. And since Vitamin A acetate is water-insoluble, the samples were diluted with ethanol to 2mL.) b) Normalized absorption of CDs, vitamin A acetate and CDs with vitamin A acetate, and the fluorescence spectrum of vitamin A acetate.

**Table S1.** Analysis parameters of the CDs for Fe<sup>3+</sup> detection.

$\lambda$ (nm)	Linear equation ( $\mu\text{mol/L}$ )	Linear range ( $\mu\text{mol/L}$ )	Correlation coefficient ( $R^2$ )	Detection limit ( $\mu\text{mol/L}$ )
426nm	$(F_0-F)/F_0=1.470\times 10^{-3}c+0.01253$	0-100	0.9975	9.6
	$(F_0-F)/F_0=1.601\times 10^{-4}c+0.1435$	100-4000	0.9964	
488nm	$(F_0-F)/F_0=1.250\times 10^{-3}c+0.009210$	0-100	0.9985	7.0
	$(F_0-F)/F_0=1.575\times 10^{-4}c+0.1181$	100-4000	0.9989	

**Table S2.** Determination of Fe<sup>3+</sup> in water sample using the proposed method.

Sample	$\lambda$ (nm)	Added ( $\mu\text{mol/L}$ )	Found ( $\mu\text{mol/L}$ , $n=5$ )	Recovery (%, $n=5$ )	RSD (%, $n=5$ )
1	426	800	771, 797, 753, 806, 781	94.2-100.8	2.7
		1000	958, 1030, 1026, 1047, 1002	95.9-104.8	3.4
		1500	1490, 1472, 1387, 1475, 1514	92.5-100.9	3.3
	488	800	755, 781, 785, 827, 818	94.4-103.3	3.7
		1000	988, 1008, 973, 1038, 973	97.3-103.8	2.7
		1500	1618, 1611, 1540, 1501, 1455	97.0-107.9	4.5
2	426	800	793, 835, 798, 751, 773	93.9-104.4	4.0
		1000	1002, 998, 989, 920, 915	92.0-100.2	4.5
		1500	1490, 1478, 1429, 1442, 1417	94.5-99.4	2.2
	488	800	786, 829, 808, 752, 756	94.0-103.6	4.2
		1000	1014, 1019, 1000, 1055, 935	93.5-105.5	4.4
		1500	1500, 1509, 1420, 1469, 1413	94.7-100.6	3.0

Sample 1: Jialing River water (taken from the Three Gorges Reservoir area of Jialing River in Beibei Dock flow region)

Sample 2: Tap water

**Table S3.** Zeta potentials vary from different pH value.

pH	6.09	7.00	8.36	9.25	10.38	11.70
Zeta potential(mV)	-1.21	-11.7	-33.6	-34.9	-35.6	-36.1



## References

- [1] Xu, Q.; Wei, J. F.; Wang, J. L.; Liu, Y.; Li, N.; Chen, Y. S.; Gao, C.; Zhang, W. W.; Sreeprasede, T. S. Facile Synthesis of Copper Doped Carbon Dots and Their Application as a “Turn-off” Fluorescent Probe in the Detection of Fe<sup>3+</sup> Ions. *RSC Adv.* **2016**, *6*, 28745-28750.
- [2] Chen, J.; Wei, J. S.; Zhang, P.; Niu, X. Q.; Zhao, W.; Zhu, Z. Y.; Ding, H.; Xiong, H. M. Red-emissive Carbon Dots for Fingerprints Detection by Spray Method: Coffee Ring Effect and Unquenched Fluorescence in Drying Process. *ACS Appl. Mat. Interfaces* **2017**, *9*, 18429-18433.
- [3] Zhu, S. J.; Song, Y. B.; Zhao, X. H.; Shao, J. R.; Zhang, J. H.; Yang, B. The Photoluminescence Mechanism in Carbon Dots (Graphene Quantum Dots, Carbon Nanodots, and Polymer Dots): Current State and Future Perspective. *Nano Res.* **2015**, *8*, 355-381.