

Supplementary Material (ESI) for RSC Advances  
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# **Polyamine-functionalized carbon nanodots: a novel chemiluminescence probe for selective detection of iron (III) ions**

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## **Experimental**

**Chemicals:** Ethylene imine polymer ( $C_{2x+4k}H_{5x+10k}N_{x+2k}$ , M.W. 1800, 99%) was obtained from Aladdin Industrial Corporation. Citric acid monohydrate ( $C_6H_8O_7 \cdot H_2O$ ) and lead chloride ( $PbCl_2$ , chemical pure) were purchased from Beijing Chemical Reagents Company. EDTA- $2Na \cdot H_2O$  was obtained from Beijing Xin Jing Ke Biotechnology Co, Ltd (Beijing, China). NaOH, HCl (36%~38%), Fe(III)chloride hexahydrate ( $FeCl_3 \cdot 6H_2O$ ), Manganese(II)chloride tetrahydrate ( $MnCl_2 \cdot 4H_2O$ ), Aluminum chloride hexahydrate ( $AlCl_3 \cdot 6H_2O$ ), Copper(II) sulfate pentahydrate ( $CuSO_4 \cdot 5H_2O$ ), Iron(II) sulfate heptahydrate ( $FeSO_4 \cdot 7H_2O$ ), Magnesium chloride hexahydrate ( $MgCl_2 \cdot 6H_2O$ ), Cobalt chloride hexahydrate ( $CoCl_2 \cdot 6H_2O$ ), cadmium chloride ( $CdCl_2 \cdot 2.5H_2O$ ), Nickel(II) nitrate hexahydrate ( $Ni(NO_3)_2 \cdot 6H_2O$ ) were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Calcium chloride anhydrate ( $CaCl_2$ ) was from Tianjin jinke chemical research institute. Mercuric chloride ( $HgCl_2$ ) was from Jiangyan universal reagents (Jiangsu, China). Purified deionised water (Millipore Milli-Q,  $\geq 18.2 M\Omega cm^{-1}$ ) was used for the preparation of all aqueous

solutions and rinsing of all laboratory ware. Stock standard solution of Fe(III) was prepared by dissolving 0.2703g FeCl<sub>3</sub>•6H<sub>2</sub>O in 10ml 0.005M HCl, both of them were prepared weekly.

### **Preparation of BPEI-Carbon Dots**

The polyamine-functionalized carbon dots (BPEI-CDs) was synthesized by the pyrolysis of citric acid and branched poly(ethylenimine) (BPEI). Firstly, 2.0g BPEI and 4.0g citric acid were dissolved uniformly with 40ml hot water in a 100ml beaker, and then the above admixture was poured into a stainless steel autoclave with a Teflon liner of 100ml capacity and heated at 195°C for 3h. Finally, the reactor was automatically cooled to room temperature. The resulting brown solution was centrifuged at 7000 rpm for 10 min to remove the weight precipitate and agglomerated particles. Then the brown aqueous solution of BPEI-CDs was dialyzed for 8h in super-purified water. The cutoff of the dialysis membrane is equal to molecular weight of 2000. Then the concentration of the acquired uniform aqueous which is about 30mg/ml was determined by freeze-dry method.

### **Instruments and characterization**

The CL kinetic curves were recorded by a BPCL Ultra-Weak Luminescence Analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China). Fluorescence measurements were performed on a FluoroMax-4 spectrofluorometer (Horiba JobinYvon, Edison, NJ, USA), using 300-500nm excitation and a slit width of 2 nm. UV-vis absorption spectra were measured on an Agilent 8453 UV-visible spectrophotometer (Palo Alto, CA, USA).

EPR spectra were collected on a Bruker spectrometer (A300-10/12, Bruker, Germany). High-resolution transmission electron microscopy (HRTEM) images were recorded by an electron microscope operating at 120 kV (JEM-2010, JEOL, Japan). Surface chemical bonding state was analyzed by X-ray photoelectron spectroscopy (ESCALAB250Xi, Thermo Scientific, USA). Fourier transform infrared (FT-IR) measurements were carried out with a FT-IR spectrometer (6100, JASCO, Japan). The CL spectra were examined by a series of high-energy optical filters (440,460, 475, 490, 505,535, 555, 575, 590, 605nm).

### **CL Measurements**

The CL kinetic characteristics of carbon dots were obtained by batch experiments, which were achieved by a static system consisted of a glass cuvette and the BPCL Ultra-Weak Luminescence Analyzer. 100 $\mu$ L of carbon dots and 100 $\mu$ L sample were added into the glass cuvette, and then NaOH was injected by a 100 $\mu$ L micro syringe from the upper injection pore.

### **Analysis of water samples**

Two river water samples and a tap water sample were collected from Qing River (Beijing, China) and our laboratory respectively. All the water samples were filtered through 0.22 $\mu$ m membrane (Millipore) and acidified with HNO<sub>3</sub> to pH 2.3. Then the CL measurements were taken to determine iron concentration within the test samples and spiked samples.

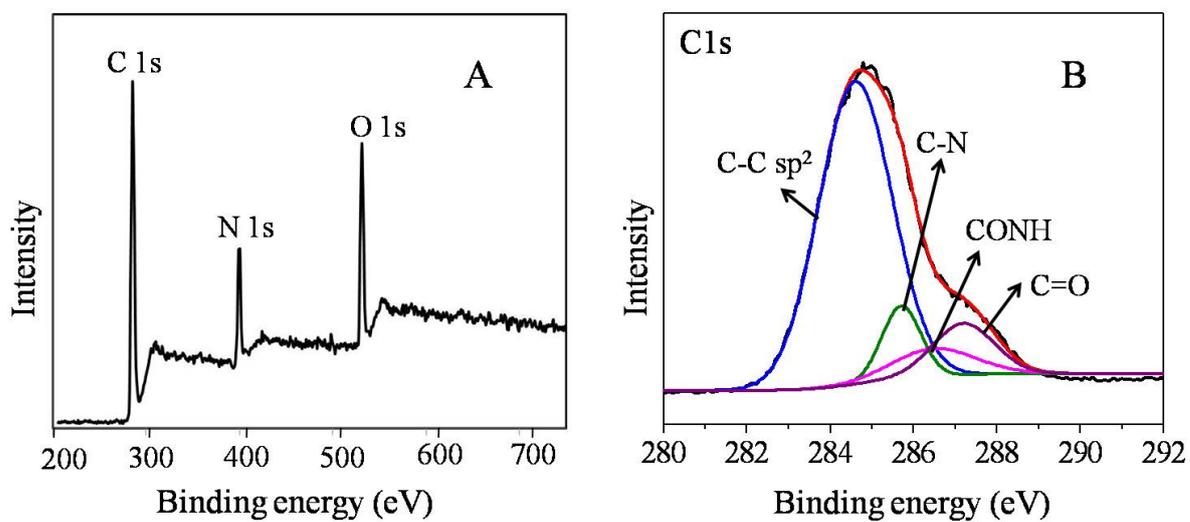


Fig. S1 XPS spectra(A) and the C1S peaks (B) of BPEI-CDs

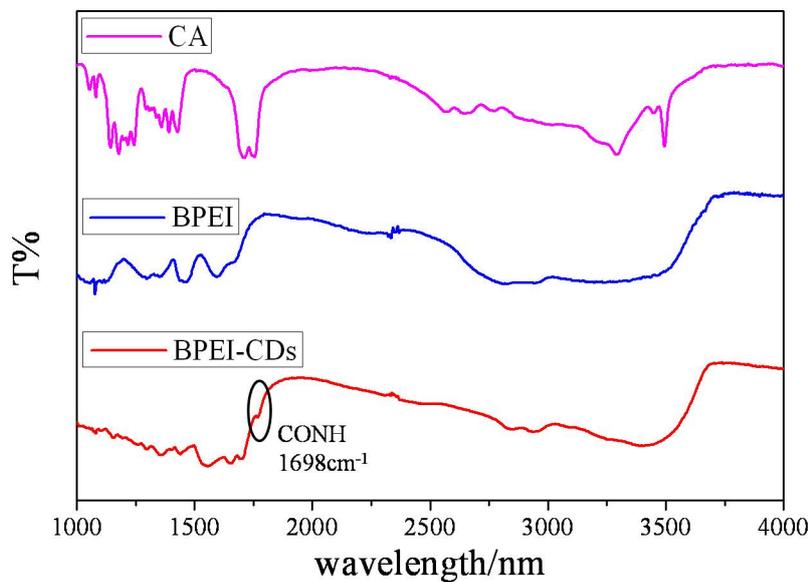
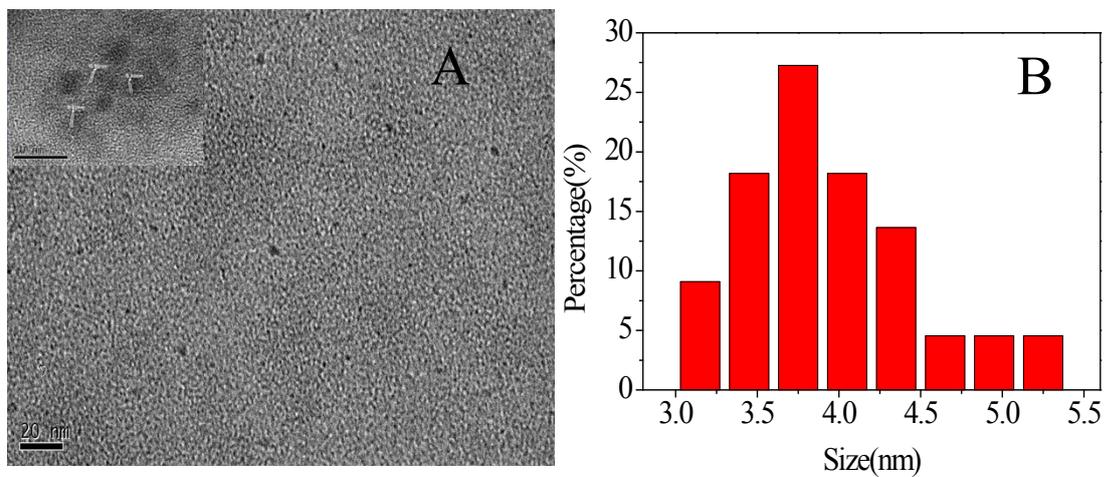
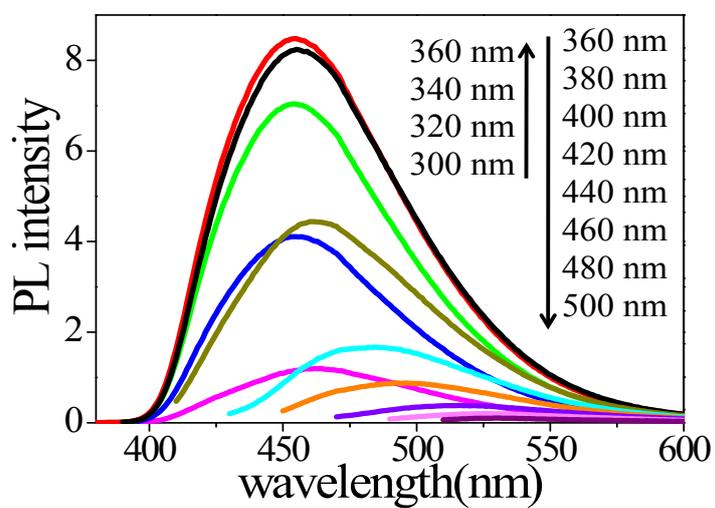


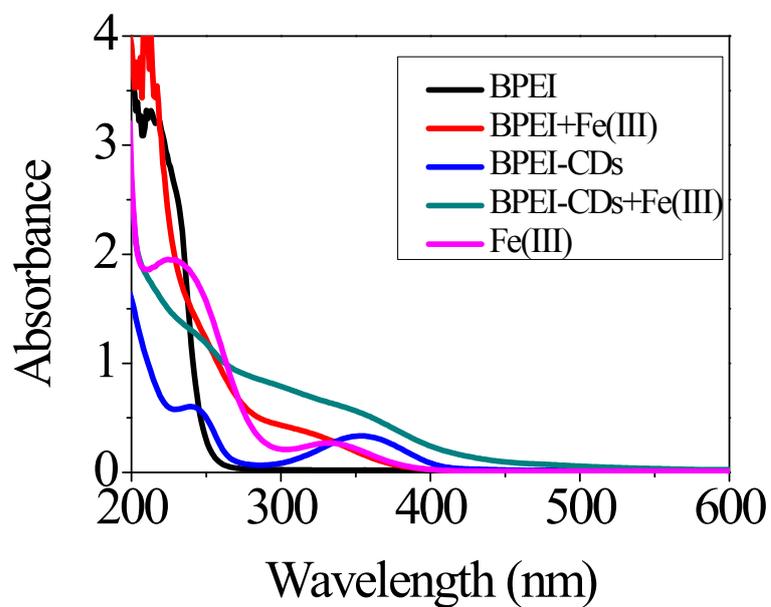
Fig. S2 FTIR spectrum of CA, BPEI and BPEI-CDs



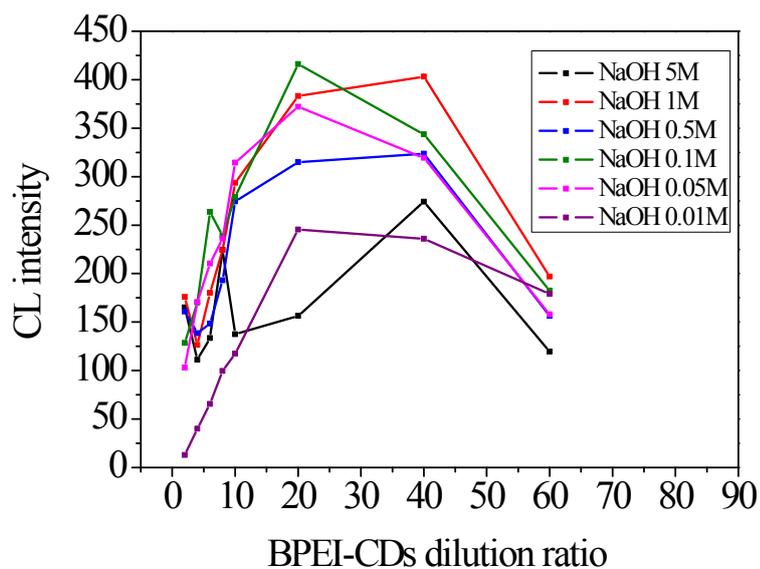
**Fig. S3** HRTEM image of BPEI-CDs (A) and the size distribution of BPEI-CDs (B)



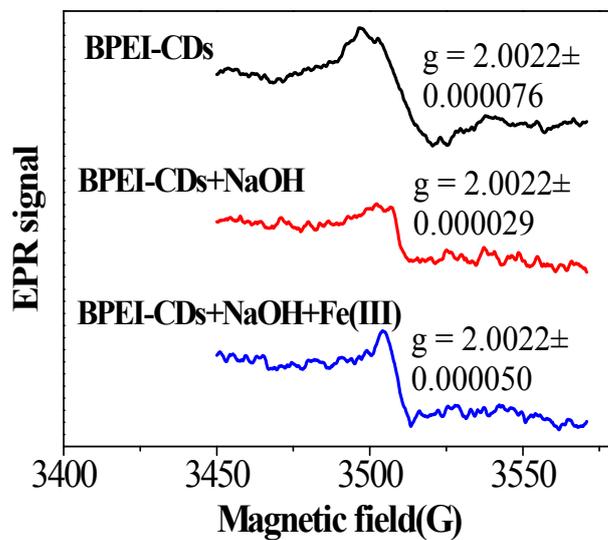
**Fig. S4** The PL spectra for BPEI-CDs excited at wavelengths from 300nm to 500nm with 20 nm increment.



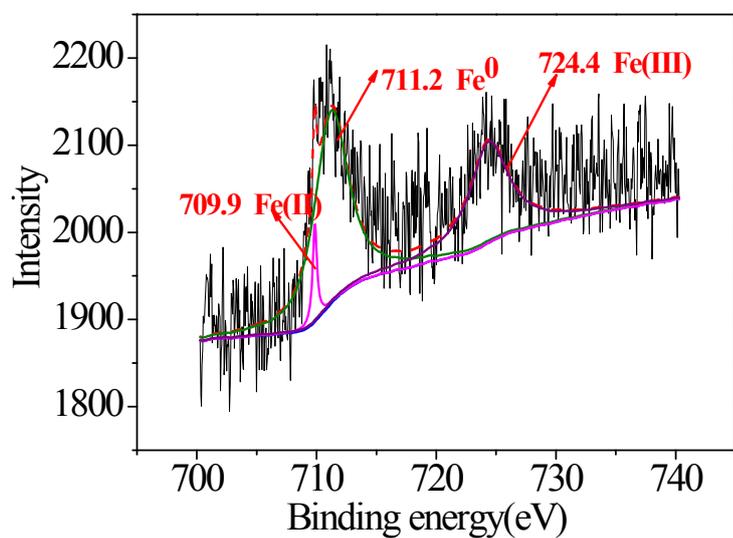
**Fig. S5** The UV-vis absorption of BPEI, BPEI+Fe(III), BPEI-CDs, BPEI-CDs+Fe(III), Fe(III)



**Fig.S6** Effect of different NaOH concentration and dilution ratio of BPEI-CDs on the improved CL intensity by Fe(III)



**Fig S7** The EPR spectrum of BPEI-CDs, NaOH-treated BPEI-CDs and BPEI-CDs after reaction with NaOH and Fe(III)



**Fig S8** Fe 2p XPS spectra of BPEI-CDs after reaction with NaOH and Fe(III).

**Table S1** Determination of Fe(III) in three water samples

<b>Samples</b>	<b>Blank (M)</b>	<b>CV% (n=3)</b>	<b>Fe(III)added (M)</b>	<b>measured (M)</b>	<b>CV% (n=3)</b>	<b>Recovery (%)</b>
Tap water	$4.25 \times 10^{-7}$	5.00	$5 \times 10^{-6}$	$5.45 \times 10^{-6}$	8.58	100.88
River 1	$4.18 \times 10^{-8}$	12.80	$5 \times 10^{-6}$	$5.24 \times 10^{-6}$	3.61	103.98
River 2	$2.87 \times 10^{-8}$	6.67	$5 \times 10^{-6}$	$4.67 \times 10^{-6}$	11.66	92.89