Supporting Information for

Synthesis of a novel cationic carbon dot and application to quantitative detection of K^+ in human serum samples

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1. Materials and Instruments

Materials

Quinaldine red was obtained from Shanghai Aladdin, Ltd. (Shanghai, China). Tetraphenylborate sodium and all metal salts (KCl, NaCl, LiCl, $BaCl_2 \cdot 2H2O$, $HgCl_2$, $CdCl_2 \cdot 2½H2O$, $ZnSO_4$, $MgCl2 \cdot 6H2O$, $CaCl_2$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). The Human Serum–Pooled was purchased from Beijing Wolcavi Co., Ltd. The other two human blood samples were collected from healthy adult volunteers at Peking University Third Hospital.

Instruments

FT-IR spectra were recorded on a Nicolet NEXUS-470 Spectrometer (Madison, USA) from KBr pellets at room temperature, using an accumulation of 32 scans and a resolution of 4 cm^{-1}, in the range of 4000~500 cm^{-1}. Samples (2 mg) were thoroughly ground with KBr and pelletized using a hydraulic press under a pressure of 600 kg/cm^2.

Fluorescence spectra were recorded on an F-7000 fluorescence spectrophotometer (Hitachi, Tokyo, Japan). All fluorescence intensity measurements were performed under the same conditions: the excitation and emission slit widths were both 5 nm, and the excitation wavelength was set at 320 nm, with a recording emission range of 340~600 nm. The photomultiplier tube voltage was set at 700 V. All ultraviolet−visible (UV-Vis) spectra were recorded on a WTF UV-2102PC UV-Vis spectrophotometer (UNICO Shanghai Instrument Co., Ltd., China).

Quantitative determination of K^+ in blood samples were recorded on an atomic absorption spectrometer (PERSEE TAS-990, Beijing, China).

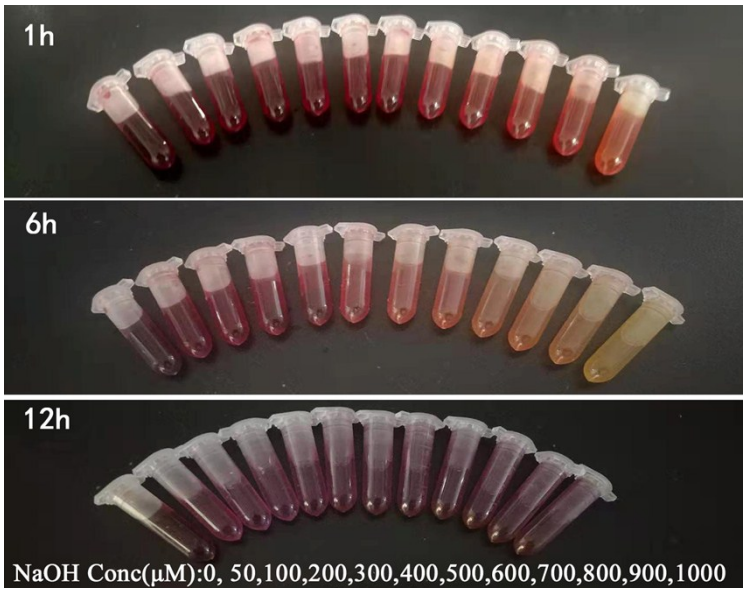
X-ray photoelectron spectroscopy (XPS) results were collected by Thermo escalab 250Xi spectrometer (USA), which uses advanced Avantage data acquisition and processing system to ensure that as much information as possible is extracted from the test data. XPS pre-processing process: appropriate amount of samples are pressed into a tablet less than 1cm.

High-resolution scanning/transmission electron microscope (STEM) (FEI Talos F200 series 200kV) was used to study the morphology of QCDs.

The data of zeta potential of samples was recorded by Mastersizer2000 Model Hydro2000SM (Malvern Instrument Ltd., UK).

2. Synthesis of QCDs

Fig. S1 QR samples at different reaction time and concentrations of sodium hydroxide



3. Quantum yield measurement

The quantum yield (Φ) of QCDs was determined by comparing the integrated fluorescent intensities (excitation at 320 nm) and absorbance values (at 320 nm) of the QCDs samples with those of quinine sulfate (standard). The quantum yield was calculated using equation (S1), where Φ is the quantum yield, k is slope, η is the refractive index of the solvent, S is the standard and X is the sample.

$$\Phi x = \Phi s\left(\frac{Kx}{Ks}\right)\left(\frac{\eta x}{\eta s}\right) \qquad \text{(S1)}$$

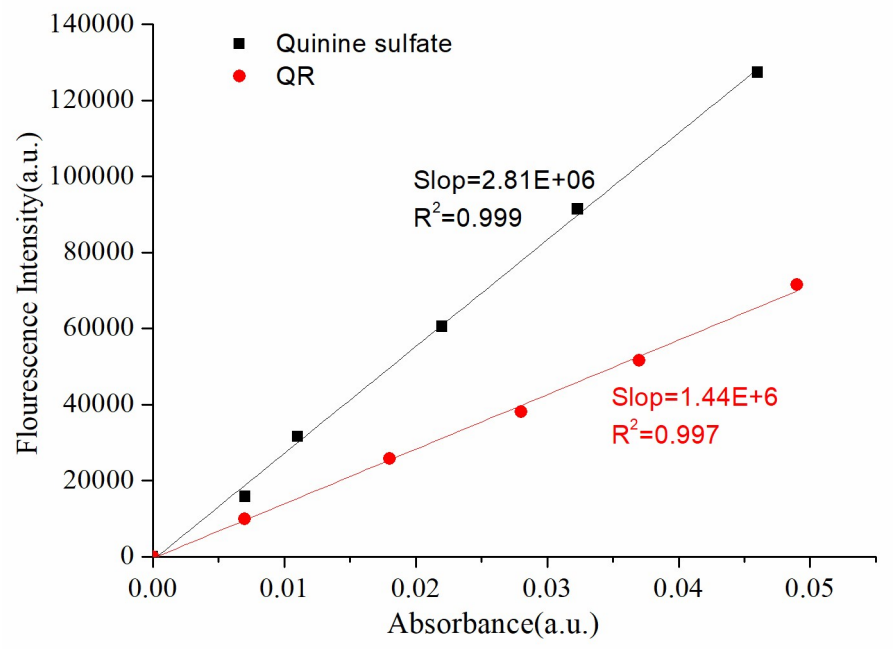
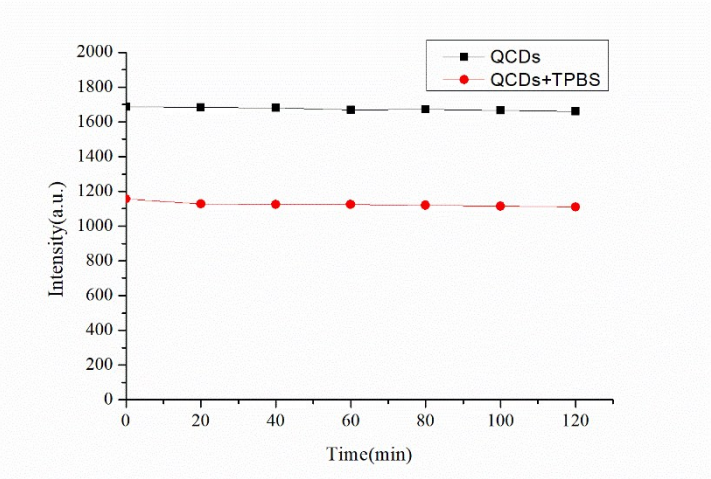


Fig. S2 Liner plots for Quinine sulfate (0.1M H_2SO_4, φ_f =0.54) and QR

4. Fluorescence stability of QCDs and QCDs+TPBS

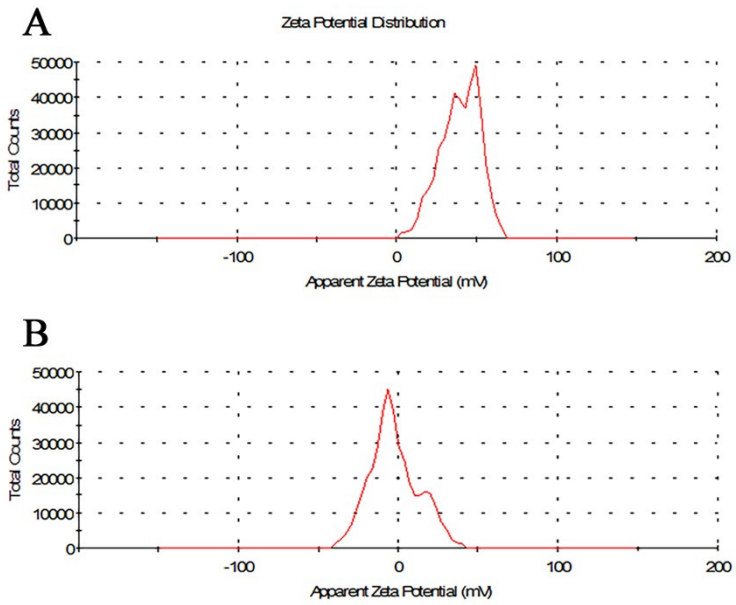
Fig. S3 The photostability of the QCDs and QCDs+TPBS measured by fluorescence



spectrophotometer every 20 min (λex = 320 nm, λem = 400 nm)

5. Zeta potentials of QRDs and QCDs+TPBS

Fig. S4 Zeta potentials of QRDs(A) and QCDs+TPBS(B)



6. Determination of the detection limit

The IUPAC recommended method was used for quantitative testing. The signal-to-noise ratio (S/N) of the detection method is first measured, and then the minimum detection limit (LOD) of the detection method is determined. The fluorescence intensity of QR was measured at a specified excitation wavelength (320 nm) and repeated 20 times, thereby obtaining the average absorbance of the blank sample and its associated standard deviation (SDblank). This SDblank is considered to be the noise (N) of our detection system. Then, a lower concentration (known) standard test sample is subjected to fluorescence emission intensity detection at a specified excitation wavelength of 320 nm. The average value (average sample) is calculated after repeating five times. Finally, S/N can be calculated by the following formula:

$$S/N = \left(average_{sample} - average_{blank}\right) / SD_{blank} \qquad (S2)$$

If the S / N result is greater than 5, the sample is diluted to half of the initial concentration, and the above S / N experimental determination is repeated until the S / N value falls within the range of 3 to 5. The concentration of the analyte satisfying 3 <S/N <5 is the LOD value.

7. Fluorescence determination of K^+ in human blood serum

The blood samples were pretreated to eliminate any protein interference and to improve the

recovery. A 3 mL portion of trichloroacetic acid (quality fraction 15%) was added to 1 mL serum to destroy the activity of proteins in the serum and to precipitate them from the solution. The mixture was centrifuged at 10 000 rpm for 10 min after vigorous shaking for 15 min. The supernatant was obtained and modulated to pH 7.0 utilizing NaOH solution. The treated serum samples were diluted 50 times using ethanol. The spiked samples were prepared by adding different K^+ solutions to the diluted serum samples then the spiked serum samples were analyzed according to the developed protocol. Standard addition and recovery experiment was carried out in the Human Serum-Pooled, and quantitative detection of K^+ was completed in all three blood samples.

Table S1 Determination of K^+ in human serum samples

plasma samples	**Added K^+(μM)**	**Found K^+ (μM)**	**Recovery(%)**	**RSD(n=3,%)**
1	5	5.05	101.07	8.11
2	10	10.83	108.36	16.54
3	20	19.17	95.86	11. 16
4	100	95.23	95.23	8.49

Table S2 Comparison of analytical performance of some assays for K^+ detection

Analysis methods	**Detection medium**	**LOD (M)**	**References**
Ion chromatography	biodiesel samples	1.1×10^{-5}	(1)
ICP-AES	human serum	6.5×10^{-5}	(2)
flame atomic absorption spectrometry (F AAS)	biodiesel samples	2.6×10^{-7}	(3)
Structure-switchingaptamers and PicoGreendye	tap water and urine samples	2.37×10^{-12}	(4)
A tricationicphenylene-ethynylene(N^{3+}) fluorophore	urine samples.	9×10^{-7}	(5)
Photoluminescence carbon dots	human serum and red blood cells	1.0×10^{-12}	(6)
Aptamer-based fluorescence	urine samples	7.5×10^{-8}	(7)

	sensor		
This work		human serum	5.7×10^{-8}

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