Ratiometric fluorescence assay based on carbon dots and Cu^{2+}-catalyzed oxidation of *O*-Phenylenediamine for the effective detection of deferasirox

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List of supplementary information

(1) Synthesis of b-CDs without post-treatment

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(1) Synthesis of b-CDs without post-treatment

A 0.1 g m-phenylenediamine (MPD) was dissolved in 10 mL acetone using ultrasound to obtain a homogeneous solution. The solution was transferred to a 50 mL hydrothermal reactor and heated at 160 ℃ for 10 h. After cooling, the product was filtered by 0.22 μm filter membrane. The filtrate was purified through dialysis for 24 h with water changed every 4 h. After lyophilization, the obtained b-CDs were stored at 4 ℃.

(2) The supplementary figures

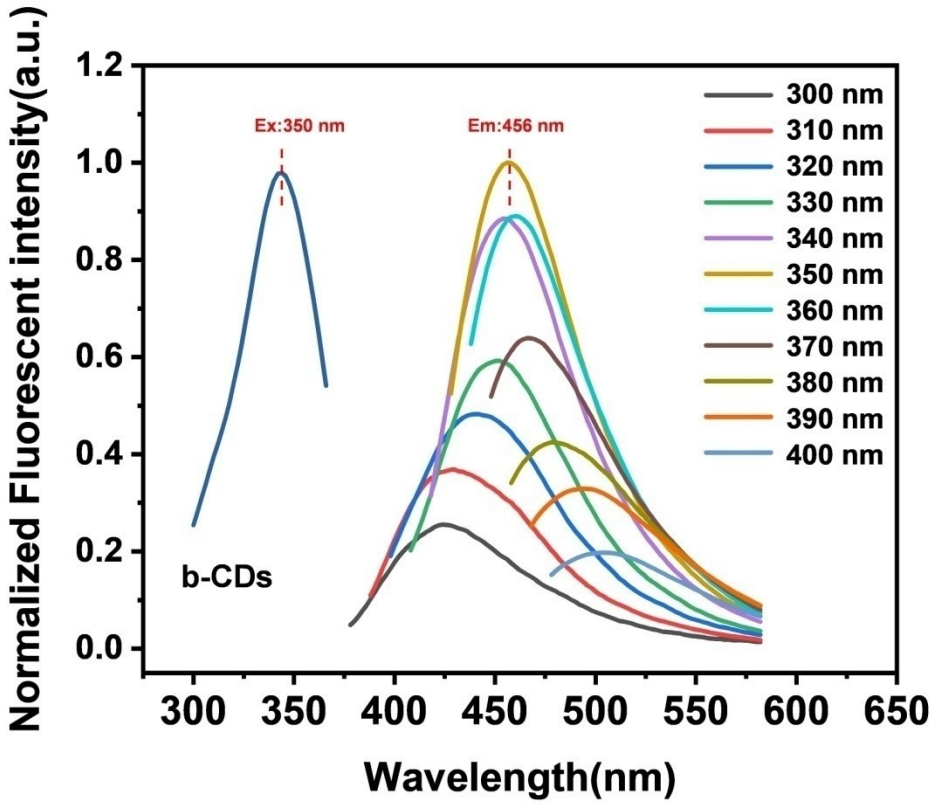

Fig. S1. The maximum excitation and emission fluorescence spectra of b-CDs with variable excitation.

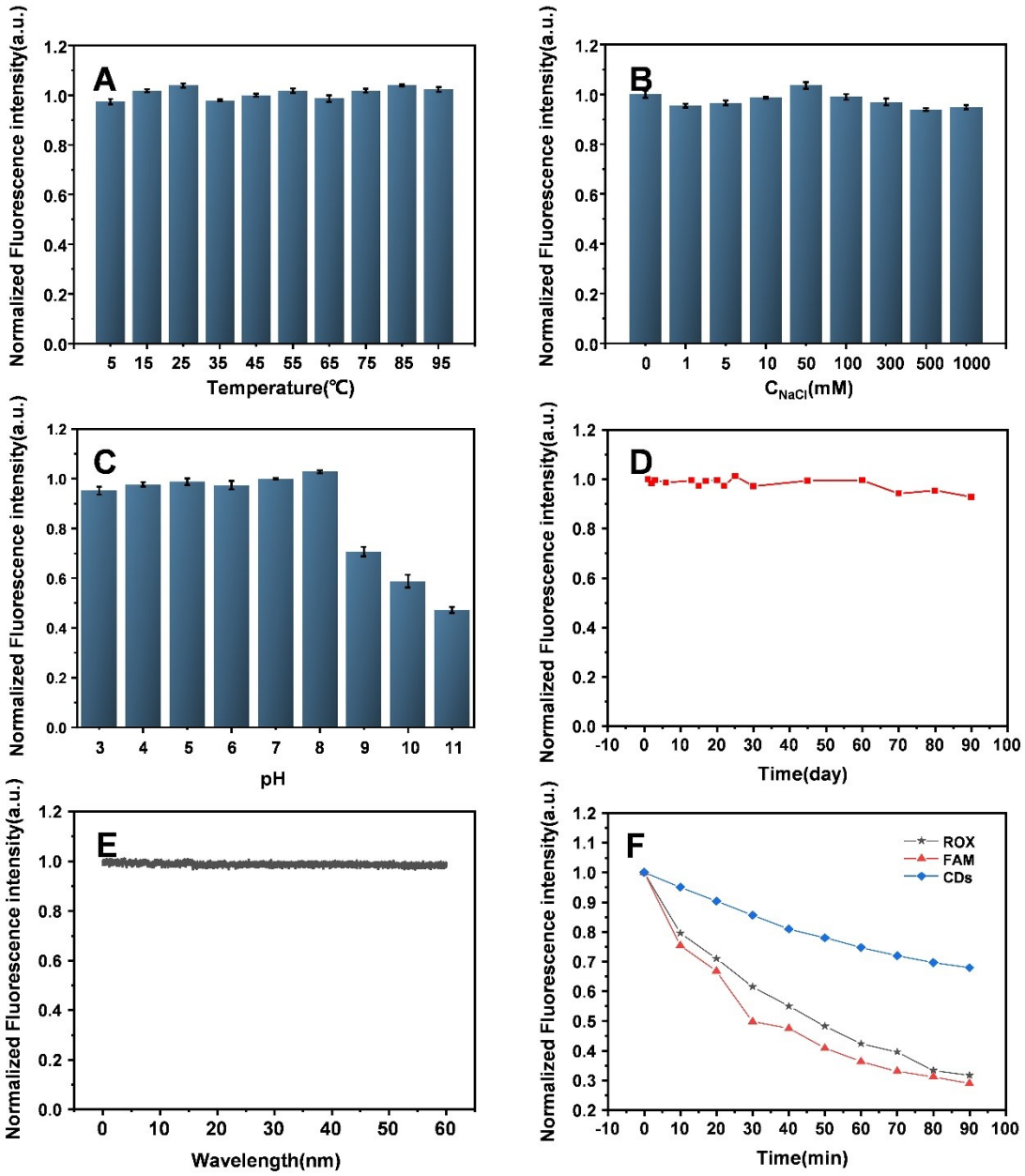

Fig. S2. The normalized fluorescence intensity of CDs at different temperatures (A), NaCl concentrations (B), pH (C), stored at room temperature for 90 days (D), continuous excitation at 370 nm for 60 min (E), and continuous irradiation at 365nm for 90 min under a 300W xenon lamp with the comparison of commercial dyes (ROX and FAM) (F).

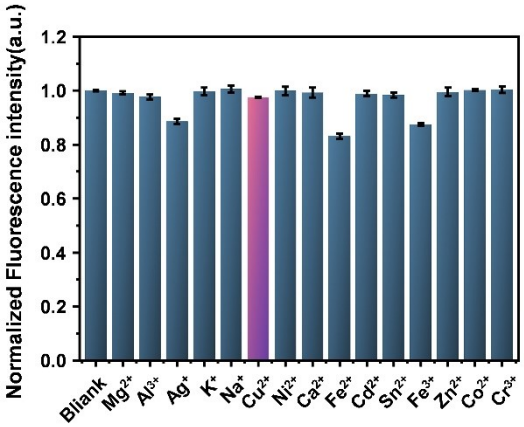

Fig. S3. Fluorescence responses of CDs to 100 μM metal ions (Mg^{2+},Al^{3+},Ag^{+},K^{+}, Na^{+}, Cu^{2+}, Ni^{2+},Ca^{2+},Fe^{2+}, Cd^{2+}, Sn^{2+},Fe^{3+}, Zn^{2+}, Co^{2+},and Cr^{3+}).

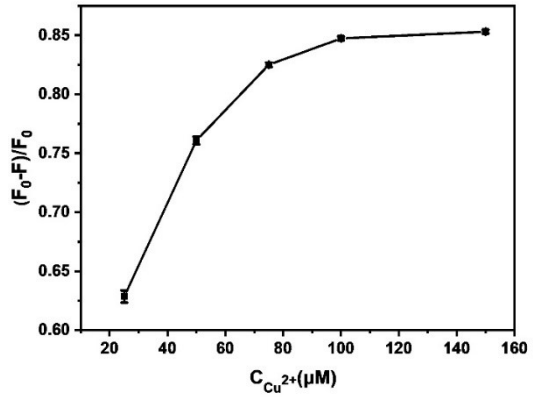

Fig. S4. The effect of the different concentrations (25, 50, 75, 100, 150 μM) of Cu^{2+} on the fluorescence intensity of the system of CDs and OPD with excitation at 370 nm. F and F_0 are the fluorescence intensity with and without Cu^{2+}, respectively.

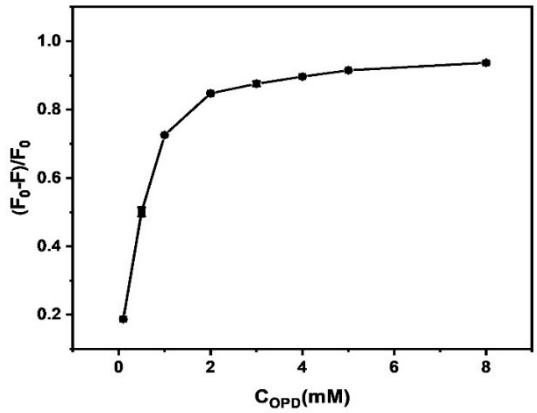

Fig. S5. The effect of different concentrations (0.1, 0.5, 1, 2, 3, 4, 5, 8 mM) of OPD on the fluorescence intensity of CDs+Cu^{2+} with excitation at 370 nm. F and F_0 are the fluorescence intensity with and without OPD, respectively.

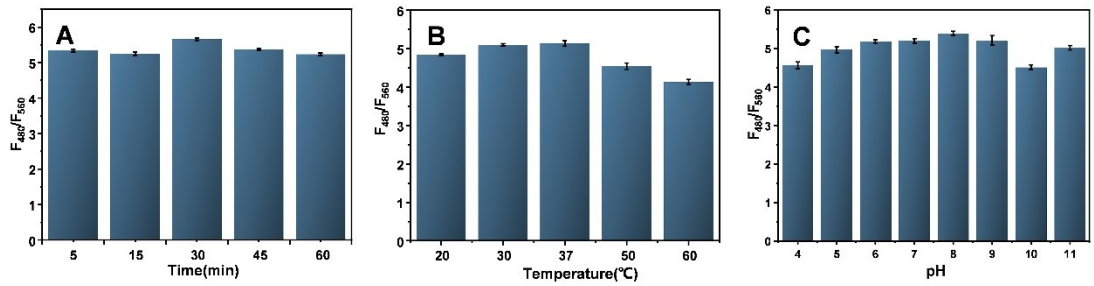

Fig. S6. The effect of the time (A), temperature (B) and pH (C) on the variable F_{480}/F_{560} in CDs-Cu-OPD with DEF. F_{480} and F_{560} represent the fluorescence intensity of CDs (480 nm) and oxOPD (560 nm), respectively

(3) The corresponding equation and the illustration of the equation for the discussion of the mechanism

$$\frac{C}{\triangle A} = \frac{1}{\triangle \varepsilon} + \frac{1}{\triangle \varepsilon K_a} \times \frac{1}{[OPD]}$$

Formula S1

C is concentration of CDs, K_a is association constant; ΔA is the change of the absorbance of CDs with and without oxOPD at λ_{416nm}, [OPD] is the concentration of OPD, and Δε is the change in absorption coefficient.

$$log\frac{F_0 - F}{F} = logK_b + nlog[OPD]$$

Formula S2

$$\frac{F_0}{F} = 1 + K_q\tau_0[OPD]$$

Formula S3

$$E = 1 - \frac{F}{F_0}$$

Formula S4

The F and F_0 are the fluorescence intensities of CDs in CDs-Cu-OPD with and without OPD, respectively; [OPD] is concentration of OPD, K_b is the binding constant and n is a number of binding sites; K_q is the steady state quenching constant and τ_0 is fluorescence decay lifetime of CDs; E is the energy transfer efficiency.

$$R_0^6 = 8.8 \times 10^{-25} K^2 N^{-4} \Phi J$$

Formula S5

K^2 is the dipole orientation factor (in fluid solution, K^2 is 2/3 for random orientation), N is the refractive index of the solvent, and Φ is the quantum yield of the CDs (Φ= 0.212), and J (J=1.38×10^{-14}cm^{-3} • L·mol^{-1}) is the spectral overlap integral between the CDs' emission and the oxOPD extinction coefficient, which was calculated from Formula 6:

$$J = \frac{\int_0^{\infty} F(\lambda)\varepsilon(\lambda)\lambda^4 d\lambda}{\int_0^{\infty} F(\lambda) d\lambda}$$

Formula S6

The λ is the wavelength, and $F(\lambda)$ is the corrected fluorescence intensity of the donor (CDs) in the wavelength range from λ to (λ+dλ) with the total intensity normalized to unity, while $\varepsilon(\lambda)$ is the molar absorption coefficient of the receptor at λ.

$$r_0 = R_0\left(\frac{1}{E} - 1\right)^{\frac{1}{6}}$$

Formula S7

The r_0 is the distance between donor and acceptor; Energy transfer efficiency (E) is calculated from Formula 4. Critical transfer distance (R_0) is calculated from Formula 5.

(4) The supplementary tables

Table S1. Detection result of DEF in Deferasirox-dispersible tablets

Specification (mg/tablet)	Measured content (mg/tablet)	Labeled percentage content (%)	RSD (n=3； %)
125	125.8	103.6	4.3

Table S2.The results of the recovery experiment of DEF in the serum samples

Serum samples	Added (μM)	Measured (μM)	Recovery (%)	RSD (n=3; %)
1	2	1.96	98.00	2.12
	4	3.86	96.50	0.730
2	4	4.09	102.3	2.82
	6	6.20	103.3	0.860

3	2	2.19	109.5	2.45
	4	4.08	102.0	0.530

Table S3. A comparison of different analytical methods for the detection of deferasirox

Analytical method	Sample matrix	Linear range (μg/mL)	LOD (μg/mL)	Ref.
CE-UV(SI-sweeping-FASS-MEKC)	plasma	1.0-20.0	0.3	1
Electrochemical (MWCNT paste electrode)	tablets and urine	0.060-6.19	0.038	2
PL(AgNPs-Tb-Deferasirox)	Urine and pharmaceutical tablets	37.3-7.5×10^4	11.2	3
PL(CDs-Cu^{2+}-Deferasirox)	tablet and plasma	0.5-20.0	0.33	4
PL(DA-CDs)	plasma	1.0-10.0	0.6	5
PL(CDs-Cu^{2+}-OPD-Deferasirox)	tablet and serum	0.5-8.0	0.38	This work
HPLC-UV(DLLME-DSS)	blood of patients with thalassemia	2.0×10^2-2.0×10^5	0.06	6
HPLC-UV(BrMmC)	Human Breast Milk	0.01–1.0	0.0026	7
HILIC/ESI/MS	plasma	0.20-120.0	0.1	8
LC/MS/MS	plasma	0.04-40	0.04	9

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